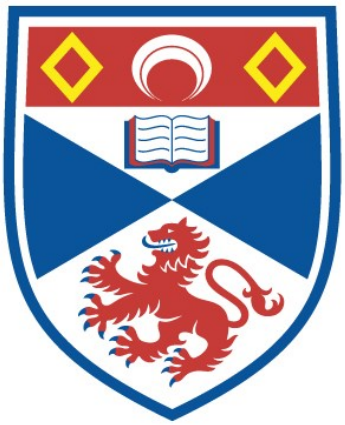
THE THERMAL DECOMPOSTION OF TRIFLUOROMETHYL IODIDE

Gordon Wylie Downs

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE THERMAL DECOMPOSITION OF TRIFLUOROMETHYL IODIDE

A Thesis presented by

Gordon Wylie Downs B.Sc.,

to the

UNIVERSITY OF ST. ANDREWS

in application for the

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March 1959.

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DECLARATION

I hereby declare the following thesis to be a record of experiments carried out by me, and furthermore, that the Thesis is my own composition and has not been previously presented in application for a Higher Degree.

The investigations were carried out in the Chemical Research Laboratories of the United College, St. Andrews, under the supervision of Dr. Charles Horrex.

UNIVERSITY CAREER

I entered the United College of the University of St.Andrews in October 1951, and graduated as a Bachelor of Science with First Class Honours in Chemistry in July 1955.

The research described in this thesis was carried out in the United College under the direction of Dr. Charles Horrex within the period August 1955 to September 1958.

CERTIFICATE

I hereby certify that Mr. G.W. Downs has spent twelve terms at research work under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

[redacted]

Director of Research.

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The Following Abbreviations and Conventions have been Used.

$D(x - x)$ = Dissociation energy of bond $x - x$

$A(x^+)$ = Appearance Potential of ion x^+

$I(x)$ = Ionisation potential for $x \longrightarrow x^+$

E_1 = Activation energy of process (1)

k_1 = Rate constant of process (1)

$\Delta H_f(x)$ = Heat of formation of x

K.cals. = 1,000 calories

e.v. = electron volts.

log = logarithm to the base 10

ln = logarithm to the base e

In rate equations, (x) = concentration of x in gm. moles/l.

Pressures quoted in "mms" are in mms. of mercury.

INTRODUCTION

There were two main reasons for deciding to investigate the pyrolysis of trifluoromethyl iodide. In the first place, it was thought that the kinetics of decomposition would be of intrinsic interest, and secondly it was hoped to derive a value of the carbon-iodine bond dissociation energy.

Several workers have investigated the decomposition of organic iodides and considerable knowledge has been obtained of their behaviour. A study of the kinetics of pyrolysis of trifluoromethyl iodide has not been published previously, indeed the substance has only been isolated within the last decade. It is one of the simpler substances in a considerable field of organic fluorine compounds which have been developed within the past few years, and there are interesting similarities and differences between these fluoro organic compounds and their hydrogen containing analogues.

It would be expected that the weakest bond, the CF_3 - I bond, would rupture first on heating giving a trifluoromethyl radical and an iodine atom. Since the pyrolysis of methyl iodide has been thoroughly investigated under a variety of conditions and found to involve methyl radicals, it was thought it would be interesting to compare the decomposition of trifluoromethyl iodide with that of methyl iodide. An extensive investigation of the pyrolysis of methyl iodide had recently been completed in St.Andrews [1,2,3] in the same type of

apparatus used in much of this work.

In this work on the decomposition of methyl iodide at low pressures, it was found that the rate of decomposition was dependent on the pressure of CH_3I and also on the pressure of inert gases; the order of the reaction was between two and one. This type of behaviour has been found in investigations of the decompositions of several simple compounds and has been explained by collision theories of unimolecular reactions. It might be expected that CF_3I , being another small and similar molecule would show these effects under similar pressure conditions. If this proved to be the case, the data would be of value for these kinetic theories. In any case, the kinetic study would be expected to give information on the reactions of trifluoromethyl radicals; these have been studied in a few recent researches and the immediate interest here is in comparison with the extensive literature on methyl radicals.

Chemical reactions involve the making and breaking of chemical bonds and a knowledge of the strengths of bonds between atoms and groups of atoms is of obvious interest from the point of view of kinetic theory. The strength of the CF_3 - I bond has been determined by several workers and the values in the literature range from 43.7 to 61 K cals/mole. It would therefore be valuable if the data obtained could lead to a decision between the competing values for D (CF_3 - I).

Before the account of the experimental work carried out, a survey is given of some published work relevant to the above two topics.

Some General Features of Free Radical Reactions.

Free gas phase alkyl radicals were first found by Paneth and Hofeditz [4] who decomposed lead tetramethyl and found that the methyl radicals produced removed a lead mirror. Since then, the decompositions of many other organic compounds have been investigated and it has been found that almost all the reactions involve free radicals. Some of these free radical reactions involve chain mechanisms in which case an observed activation energy for the reaction will be composite and will not be directly identifiable with any bond energy. The Rice-Herzfeld mechanism for the decomposition of hydrocarbons is a well known example of this, and in free radical reactions the mechanism has to be elucidated completely in order to allow a bond energy to be determined.

The precise study of the individual reaction steps in free radical reactions is difficult because of the trouble in measuring radical concentrations. The reactions of radicals have been investigated mainly by the use of a comparative method in which the rate of dimerisation of a radical is compared with the rate of some other reaction involving the radical. By this means, it has been fairly well established that the activation energies for the attack of radicals on molecules are low.

The other factor which controls the value of a reaction rate constant is the value of the pre-exponential factor in the expression for the temperature dependence of the rate constant. Kinetic theory

calculations would indicate a collision rate, Z, of about 10^{10} to 10^{11} $l.mole^{-1}sec^{-1}$. The value of k is given by

$$k = p Z e^{\frac{-E}{RT}}$$

where p is the steric factor and was introduced to account for temperature independent factors much less than the collision frequency. There is much data on the values of p [5] and several theoretical attempts have been made to calculate it.[6,7]. It seems that as the complexity of the attacking radical R increases, so the value of p decreases. Values of p for the reactions of atoms with molecules would appear to be of the order of 10^{-1} and it is fairly well established that for hydrogen abstraction reactions by methyl radicals that p is about 10^{-4}. [8,9]. However, Szwarc and Roberts[10] found that p for the attack of a methyl radical on toluene is not less than 0.1 and values of p from 2.10^{-5} to 6.10^{-5} have been found by Ayscough and Steacie[11] for hydrogen abstraction reactions of CF_3 radicals.

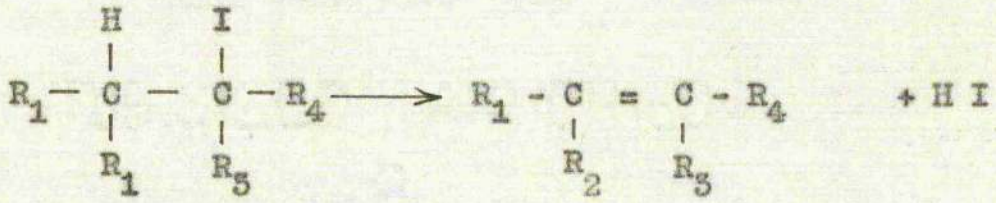
The values of steric factors in second order reactions are of interest in some of the reaction steps in the pyrolysis of CF_3I.

The Decompositions of Organic Iodides.

Carbon-iodine bonds are relatively much weaker than carbon-carbon and carbon-hydrogen bonds, so it might be expected that the first bond to break on heating an organic iodide would be the carbon-iodine bond. All organic iodides show continuous absorption in the region around 2,500 to 2,700 Å and this has been interpreted as being due once again

to the breaking of the C - I link. It is interesting to note, however, that attempts to correlate the long wavelength limit of absorption with D (R - I) as determined by independent methods have not been very successful.

The primary step in the decomposition of most organic iodides has been interpreted from the kinetics as being the breaking of the R - I bond. The only other reasonably likely first step is the decomposition into hydrogen iodide and an olefine. The dissociation into a radical and an iodine atom involves only the stretching and eventual breaking of a carbon iodine bond and the energy for this process will be D (R - I). The decomposition into HI and an olefine is a more complicated process. Consider the reaction



For this reaction to proceed, the C - H and C - I bonds have to be stretched and the hydrogen and iodine atoms have to come within bonding distance of one another. The energy for this process will be difficult to calculate, but most experimental evidence indicates that the reaction is much less likely than the simple split into a radical and an I atom.

There are some iodides for which decomposition into an olefine and hydrogen iodide is impossible because no hydrogen atom is available on an adjacent carbon. Methyl iodide, benzyl iodide and

phenyl iodide come into this category as does of course trifluoromethyl iodide. Indeed, the decompositions of perfluoroiodides might well prove to have simpler kinetics than the decompositions of normal iodides since no complications should arise due to the formation of interhalogen compounds analogous to the production of HI. At the other extreme, the main reaction in the pyrolysis of tert-butyl iodide [12] is the decomposition to give iso-butylene and hydrogen iodide. Between these limiting cases are the decompositions of many other iodides in which a little HI is found among the products. This HI can be produced either by an initial split into an olefine and HI occurring to some extent, or by secondary reactions of iodine atoms and alkyl radicals.

It is convenient to list the possible reactions which can occur and then to examine how far these predictions are fulfilled by the experimental evidence.

If the initial split is into an olefine and hydrogen iodide only, provided that the olefine is stable, almost the only possible secondary reaction which can occur is the addition of HI to the olefine. This is the case with tert-butyl iodide where an equilibrium is set up. When the primary step is a split into a radical, R, and an I atom, the complete reaction mechanism will consist of several of the following steps:-

a) The radical may react with iodine atoms or molecules to reform RI.

b) Two radicals can dimerize to form R - R or can disproportionate to

give an olefine and a paraffin.

c) The radical, R, may attack the parent iodide RI according to

either $$R + RI \longrightarrow R-R + I$$

or $$R + RI \longrightarrow RH + R'$$

where R' is a radical containing an iodine atom

The radical, R', may decompose to give an iodine atom and an olefine or it may react with a radical or atom to give a stable molecule.

d) Iodine atoms will take part in the equilibrium

$$I + I \rightleftharpoons I_2$$

e) Reaction between an iodine atom and the parent compound RI may take place according to

$$I + RI \longrightarrow R + I_2$$

f) The iodine atom may react with a radical to produce an olefine and HI

g) If the radical has not reacted in some other way, it may decompose to yield an olefine and a hydrogen atom. This hydrogen atom may then attack the parent iodide to form HI and the radical R or it may react with iodine to form HI.

When HI is produced either as a result of the direct decomposition of the iodide, or from secondary reactions, the additional reaction

$$R + HI \longrightarrow RH + I$$

may take place.

Evidence for many of these types of reaction step may be obtained from the extensive investigations on the photolysis of methyl iodide.

Methyl iodide is the simplest organic iodide and it might be thought that its decomposition would be fairly straightforward. Several workers[13,14] found that the quantum yield was very low, due presumably to the efficiency of the back reaction, and West and Schlessinger[15] proposed the following mechanism to account for the kinetics and the observed products.

$$CH_3I + h\nu \longrightarrow CH_3 + I \quad (1)$$

$$CH_3 + I \longrightarrow CH_3I \quad (2)$$

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I \quad (3)$$

$$CH_2I + I \longrightarrow CH_2I_2 \quad (4)$$

$$CH_2I + CH_3 \longrightarrow C_2H_5I \quad (4a)$$

$$CH_2I + CH_3I \longrightarrow CH_2I_2 + CH_3 \quad (5)$$

$$CH_2I_2 + h\nu \longrightarrow CH_2 + I_2 \quad (6)$$

$$2\,CH_2 \longrightarrow C_2H_4 \quad (7)$$

$$CH_2 + CH_3I \longrightarrow C_2H_5I \quad (8)$$

$$2\,CH_3 \longrightarrow C_2H_6 \quad (9)$$

$$2\,I + M \longrightarrow I_2 + M \quad (10)$$

Some attention has been given to the problem of stopping the back reaction in an attempt to simplify the kinetics. Nitric oxide[16], silver[15, 17], and hydrogen iodide[18] all proved capable of doing this, at least to some extent. The formation of "hot" methyl radicals has been suggested[17, 19, 20] to account for the reaction

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I.$$

Ogg and his collaborators pyrolysed a number of organic iodides

in static systems and the results obtained illustrate how different kinetic behaviour may arise due to different elementary reaction steps occurring. The iodides studied were n-propyl[21], iso propyl[22], n-butyl[21], sec-butyl[25], iso butyl[24], t-butyl[12] and ethylene iodide[25]. Hydrogen iodide was formed in the case of iso-propyl, n-butyl, sec-butyl, iso butyl and t-butyl iodides. Only in the case of t-butyl iodide was it certain that the primary step was a split into HI and an olefine, though in the case of isopropyl iodide, the kinetics could be explained by assuming this as the initial step.

For all the iodides of the formula $C_nH_{2n+1}I$ except t-butyl iodide, the decomposition was given by the equation

$$2\ C_nH_{2n+1}I \longrightarrow C_nH_{2n} + C_nH_{2n+2} + I_2$$

but the mechanisms and rate equations varied widely. In the cases of n-propyl and iso-butyl iodides, the main iodine producing reaction was iodine catalyzed and the rate was given by the expression

$$-\frac{d(RI)}{dt} = k\ (RI)\ (I_2)^{\frac{1}{2}}$$

Part of the decomposition of sec-butyl iodide and ethylene iodide was also iodine catalyzed and the rate obeyed the expression

$$-\frac{d(RI)}{dt} = k_1\ (RI) + k_2\ (RI)\ (I_2)^{\frac{1}{2}}$$

Iso propyl iodide gave first order kinetics

$$-\frac{d(RI)}{dt} = k\ (RI).$$

Detailed considerations of the possible reaction mechanisms are given in the original papers and have been reviewed by Steacie[8].

Other studies have shown more clearly the existence of individual reaction steps or have demonstrated how the extent of a reaction step varied from compound to compound. Jungers and Yeddanapalli[26] investigated the photosensitization of ethylene polymerization by a series of alkyl iodides and found an increase in the effectiveness in the order methyl, ethyl, n-propyl, iso-propyl iodide. This is presumably due to a decrease in the same order of the efficiency of the reaction $R + I \longrightarrow RI$, possibly on steric grounds.

The effect of the attack of a radical on the parent iodide is illustrated by the decomposition of allyl iodide[27] which is said to proceed according to the mechanism

$$CH_2=CHCH_2I \rightleftharpoons CH_2=CHCH_2 + I$$

$$I + I \rightleftharpoons I_2$$

$$CH_2=CHCH_2 + CH_2=CHCH_2I \longrightarrow \text{diallyl} + I$$

In the case of benzyl iodide, a radical is produced which is resonance stabilised, which cannot readily decompose and which does not attack the parent compound. The reaction has been investigated by Horrex and Szwarc[28] and by Gow and Horrex[29] and the mechanism found to be

$$C_6H_5CH_2I \rightleftharpoons C_6H_5CH_2 + I$$

$$C_6H_5CH_2I + I \rightleftharpoons C_6H_5CH_2 + I_2$$

$$I + I \rightleftharpoons I_2$$

$$2\,C_6H_5CH_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

The rate determining step is therefore the formation of dibenzyl.

Radioactive iodine has been used in elegant thermal and photochemical studies on organic iodides in inert solvents by Noyes. The mechanisms deduced from the results illustrate which elementary reaction steps are likely to be involved in the breakdown of the iodides investigated. Iodine atoms have been found to take part in the exchange between radioactive iodine and ethylene iodide[30], allyl iodide[31], benzyl iodide[32] and sec butyl iodide[33]. It was proved that free radicals were involved in the exchanges with allyl and benzyl iodides and that the reaction steps

$$R + I_2 \longrightarrow RI + I$$

$$I + RI \longrightarrow R + I_2$$

must occur for the cases $R = CH_2 = CHCH_2$

or $R = C_6H_5CH_2$

The attack of an iodine atom upon a radical to give HI and an olefine has been shown in the photolysis of ethyl iodide[34] where the reaction

$$I + C_2H_5 \longrightarrow C_2H_4 + HI$$

occurs. It has also been found that an iodine atom will attack a cyclohexyl radical to give cyclohexene and HI[20].

Lossing and his collaborators have shown the presence of free radicals in the decompositions of many iodides by use of the mass spectrometer and have in fact used some of the iodides as sources of radicals for ionization potential measurements. Methyl radicals have

been found in the pyrolysis of CH_3I[35], allyl radicals in the pyrolysis of allyl iodide and benzyl radicals in the pyrolysis of benzyl iodide[36]. Free methyl radicals have also been found in the pyrolyses at high temperatures of ethylene iodide, iso propyl iodide and n-propyl iodide.[35] In the case of the last two, no free propyl radicals were found and the methyl radicals which were detected may result from the breakdown of propyl radicals at the high temperatures used.

In an attempt to simplify the decompositions of organic iodides, the fast flow technique developed by Rice in his investigations on free radicals was extended by Butler, Mandel and Polanyi[37] to the thermal decompositions of iodides at low pressures. By the use of low pressure of reactant, small percentage decomposition and short contact time, they hoped to reduce the amount of secondary reaction and to measure the rate of initial split

$$R\,I \longrightarrow R + I$$

The extent of reaction was measured by the iodine produced and they interpreted their results in terms of a first order rate constant $\underline{k}$. From the temperature dependence of $\underline{k}$ or from the equation

$$k = 10^{13}\, e^{-E/RT}$$

they worked out activation energies for the decompositions and identified these with the C - I bond dissociation energies. Their work aimed at a broad survey in order to see if the bond energies derived in this manner agreed with other data, and to obtain an indication of the variation of D (C - I) with structure. No detailed

investigations of the kinetics of decompositions were made.

One of the iodides which was pyrolysed using this technique was methyl iodide. Only five experiments are quoted by Butler and Polanyi and they did not carry a full investigation. This work was continued and elaborated by Horrex and Lapage[1,2] and Horrex and Cundall[3]. The decomposition was examined in flow systems at both high and low pressures. At low pressures, i.e. up to 1 mm. CH_3I and 15 mms. carrier gas, the reaction could be described by the stoichiometric equation

$$4\ C H_3 I \longrightarrow 3\ C H_4 + C + 2\ I_2$$

Under these conditions, the rate was found to be sensitive to the pressure of $C H_3 I$ and to the pressure of inert gases; this was explained on the collision theories of unimolecular reactions. No back reaction could be detected by the addition of iodine to the system, the methyl radicals being removed on the wall to form carbon and methane. At these low pressures, the rate was second order in $C H_3 I$ concentration.

In order to obtain conditions where the rate was first order in $C H_3 I$, a high pressure flow system was used in which there were 1 to 5 mms of $C H_3 I$ in a stream of N_2 at 600 mms. pressure. Under these conditions, there was found to be a back reaction and this was prevented by injecting about 7 mms of toluene into the gas stream. The reaction may be represented by

$$C H_3 I \longrightarrow C H_3 + I$$

$$C H_3 + C_6 H_5 C H_3 \longrightarrow C H_4 + C_6 H_5 C H_2$$

$$2\, C_6H_5 C H_2 \longrightarrow C_6 H_5 C H_2 C H_2 C_6 H_5$$

The reaction under these conditions was first order in $C H_3 I$ and the temperature dependence was given by $k = 2.6.10^{13} \exp \frac{-54,700}{RT.}$

The activation energy of 54.7 K cals/mole was identified with $D (CH_3 - I)$.

The only other pyrolysis of $C H_3 I$ quoted in the literature appears to be that by Ogg[58] who studied the decomposition of $C H_3 I - H I$ mixtures in a static system. He proposed the following mechanism with the indicated thermal changes

$$C H_3 I \longrightarrow C H_3 + I \qquad - 45 \text{ K cals}$$

$$C H_3 I + H I \longrightarrow C H_4 + I_2 + 16 \text{ K cals}$$

$$C H_3 + HI \longrightarrow C H_4 + I + 24 \text{ K cals}$$

$$C H_3 + I_2 \longrightarrow C H_3 I + I + 8 \text{ K cals}$$

$$2 I + M \longrightarrow I_2 + M$$

This gives

$$\frac{d (I_2)}{dt} = k_1 (CH_3 I) (HI) + k_2 \frac{(C H_3 I) (HI)}{(HI) + (I_2)}$$

where k_1 and k_2 are constants. His value of $D (CH_3 - I)$ is now regarded as being about 12 K cals too low and suggests his mechanism is not reliable.

Some Previous Work on CF_3I

Haszeldine and his co-workers who, in 1948, isolated CF_3I[39], have investigated many of the reactions of this compound. Most of the work, however, has been concerned with the nature of the products and the mechanisms of their production and not with detailed kinetic studies of the processes. In an investigation of the photolysis, Barnus, Emeleus and Haszeldine[45] found that the quantum yield was less than .002, and that the products were C_2F_6, I_2 and a little SiF_4, the latter resulting from attack of CF_3 radicals on the silica reaction vessel. Addition of oxygen, cyanogen, chlorine, ethylene, carbon tetrachloride, water, ethyl alcohol or n-hexane increased the quantum yield; in the last three cases, CF_3H was formed. It was concluded that the primary process was a split into CF_3 radicals and I atoms, that the low quantum yield was due to back reaction to reform CF_3I, and that the addition of any material which would react with either CF_3 radicals or I atoms, and thus prevent the back reaction, increased the quantum yield.

When CF_3I is irradiated or heated in the presence of C_2H_4 or C_2F_4, short polymers of the type $CF_3(CH_2)_nI$ and $CF_3(CF_2)_nI$ respectively are formed[46], and with C_2H_2, short polymers of the general formula $CF_3(CH=CH)_nI$ are produced[47]. Haszeldine has elaborated this work, using the reactions of perfluoroalkyl radicals to synthesise fluorinated molecules. Some work has been done by Henne and his collaborators on the direction of addition of CF_3I to

unsaturated compounds[48].

Dacey[49] photolyzed CF_3I but at much lower pressures than Haszeldine and found quantum yields from .02 to .15, the yield increasing as the pressure of CF_3I was decreased. The products up to a pressure of 10 mms. were I_2 and C_2F_6 in the ratio 1 : 1 and above this pressure, some C_2F_4 was found. Nitric oxide and silver increased the yield and he concluded the mechanism was:-

$$CF_3I + h\nu \longrightarrow CF_3 + I$$

$$CF_3 + I \longrightarrow CF_3I$$

or $$CF_3 + I_2 \longrightarrow CF_3I + I$$

$$2\,CF_3 \longrightarrow C_2F_6$$

No CF_4 was found, so the reaction

$$2\,CF_3 \longrightarrow CF_4 + CF_2$$

cannot occur.

The reaction of CF_3I, CF_3Br and CF_3Cl with sodium in a Polanyi type sodium flame apparatus has been studied by Hodgins and Haines[50]. They found the primary reaction to be

$$CF_3X + Na \longrightarrow CF_3 + Na\,X$$

and the activation energies for this reaction to be 1.7, 2.5 and 7.4 K cals/mole for CF_3I, CF_3Br and CF_3Cl respectively. When hydrogen was used as a carrier gas, CF_3H was formed; C_2F_6 and a considerable proportion of C_2F_4 were also produced, both when using H_2 and He as carrier gases. It was suggested the C_2F_4 resulted from

$$CF_3 \longrightarrow CF_2 + F$$

followed by $2\,CF_2 \longrightarrow C_2F_4$

or from $2\,CF_3 \longrightarrow C_2F_4 + F_2$

However, it is not impossible that the reactions

$$Na + CF_3 \longrightarrow CF_2 + NaF$$

$$2\,CF_2 \longrightarrow C_2F_4$$

might occur and produce the C_2F_4. No CF_4 was found.

Some electron impact work has been done on CF_3I, but as this was concerned with the determination of D (CF_3 - I) and not with kinetics, it is discussed in the section on the bond energy of CF_3-I.

Other Reactions Involving CF_3 Radicals.

Some work has been done on CF_3Br and CF_3Cl. CF_3Br has been pyrolysed using the toluene carrier technique[51], but H Br was the only reaction product analyzed; from this work D (CF_3 - Br) has been deduced to be 64.5 K cals/mole. The pyrolysis of CF_3Cl has been examined in an alumina vessel[52]. The products were CF_4, CF_2Cl_2, CO_2 and Cl_2 but the reaction was complicated by attack on the walls of the vessel. Rabinowitch and Reed[53] reacted sodium atoms with the series of compounds CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl. Based on D (CH_3 - Cl) = 81.2 K cals/mole[54], they obtained D (CF_3 - Cl) = 79.5 $\pm$ 2 K cals/mole.

Steacie and his co-workers have used CF_3COCF_3 as a source of CF_3 radicals in photolysis experiments. The photolysis of CF_3COCF_3 alone produces only C_2F_6 and CO ; no CF_4 is found and the

reaction $CF_3 + CF_3COCF_3 \longrightarrow C_2F_6 + CF_3CO$ does not occur[55]. The energies of activation for reactions of the type

$$C F_3 + R H \longrightarrow C F_3H + R$$

have been measured[56] and Ayscough[57] has found that E for the reaction

$$C F_3 + C F_3 \longrightarrow C_2 F_6$$

is less than 1.5 K cals/mole, and is zero if the steric factor for the reaction is assumed to be 0.16.

Sieger and Calvert[58] have photolyzed CF_3COCH_3 in order to compare the reactions of CF_3 and CH_3 radicals in the one system. They suggest that the higher rate of abstraction of H by CF_3 radicals may be due to the fact that there is an energy of activation for their recombination.

Hexafluoroazomethane has also been used as a source of CF_3 radicals. Photolysis produced CF_3 radicals which added on to the parent compound, but it has been possible to deduce that $D(CF_3 - H) = D(CH_3-H) - 0.5$ K cals/mole[54]. Pyrolysis of $CF_3N{=}NCF_3$ has yielded CF_3 radicals, the ionization potential of which has been found to be 10.10 v. using a mass spectrometer[60].

The photolysis of CF_3CHO has been studied by Dodd and Smith[61]. The products were CF_3H, C_2F_6 and CO. Quantum yields of CF_3H and CO of up to 60 indicated a chain mechanism involving CF_3 radicals produced in the initial step; they found that the association of CF_3 radicals was independent of total pressure down to 0.5 mms. Mercer and Pritchard[62] attempted to use the toluene carrier technique

to find D ($F_3C - CF_3$). CF_3 radicals were produced, but the experiments were complicated by decomposition of the toluene. The attack of CD_3 radicals on CF_3H produces CF_3 radicals by the reaction[65]

$$C D_3 + C F_3 H \longrightarrow C D_3 H + C F_3$$

Margrave and Wieland[64] have also found the radicals CF_2 and CF in the decomposition of CF_4 under equilibrium conditions in a graphite tube.

It is interesting that in all this work, no CF_4 has been found, showing that the fluorine abstraction reaction

$$C F_3 + R F \longrightarrow C F_4 + R$$

does not occur readily.

The Attack of Fluorinated Radicals on Glass and Silica.

Work involving fluorinated radicals is complicated by the fact that the radicals may react with glass or silica to produce $Si F_4$, COF, CO_2 and occasionally CO. The extent of this attack seems to vary with the source of the radicals[65]. Dodd and Smith[61] found no trace of attack up to about 400°C, while Ayscough and Steacie[55] found that $Si F_4$ and CO_2 were such a large proportion of the reaction products at 350°C, that they did not work above this temperature. These workers resorted to sputtering CaF_2 on the reaction cell to reduce attack. Farmer et alia[60] tried to reduce the attack of CF_3 radicals from the pyrolysis of $H_g (CF_3)_2$ by coating the reactor with aquadag.

Other workers have constructed reaction vessels from materials

other than silica and glass. Trenwith and Watson[52] in a study of the pyrolysis of the chlorofluoromethanes used an alumina tube, but this was not immune from attack at the highest temperatures used. A reaction vessel made from phosphate glass was used by Stewart and Cady[66] in a study of the decomposition of CF_3COOF. This glass appeared resistant to chemical attack, but it was not mechanically strong and was subject to thermal strains. Platinum, silver and carbon tubes have been employed and appear satisfactory[67].

Atkinson and his co-workers[68] used nickel and stainless steel vessels for the pyrolysis of C_2F_4. Fluorides of manganese, chromium and iron were formed in the stainless steel vessel, only the nickel and titanium components remaining unattacked. The nickel vessel, however, appeared satisfactory, and they found homogeneous gas phase reactions occurring in it.

Elementary fluorine can be handled in nickel and a nickel vessel was used for the preliminary work in the present investigation.

From the results of this work with CF_3 radicals and from the present investigation, it is possible to suggest the causes of the apparent discrepancies in the attack of CF_3 radicals on glass and silica. Attack on the reaction vessel would appear to depend on the stationary concentration of CF_3 radicals. When some easy reaction path is open to the CF_3 radicals, their concentration will be low; this is the case in the work on CF_3CHO where the CF_3 radicals readily abstract hydrogen from the parent aldehyde, and in the work on

$CF_3N = NCF_3$ where CF_3 radicals add on to the parent compound. In neither case is there attack of radicals on the wall. In the present investigation, it was possible for CF_3 radicals to react with iodine, toluene or hydrogen iodide and once again there was no serious attack on the glass.

However, in the decompositions of CF_3COCF_3 and of $Hg(CF_3)_2$, the only reaction open to a CF_3 radical was abstraction of a fluorine atom or a CF_3 radical to give CF_4 or C_2F_6 respectively. These reactions appear to be very difficult and do not occur readily; there is therefore in these cases a high stationary concentration of CF_3 radicals and attack on the wall occurs.

It would appear that the activation energy for the attack of a CF_3 radical on glass or silica is such that the reaction proceeds at a measurable rate above about 500°C.

Unimolecular Reactions.

A first order reaction is one in which the rate of reaction is proportional to the concentration of reactant.

$$\frac{-d(A)}{dt} = k\,(A)$$

Although the rate depends on the first power of reactant concentration, activation of the molecules takes place by a collision process. The first simple theory about the mechanism of the activation process was put forward separately by Christiansen[69] and Lindemann[70]; Hinshelwood has been prominent in the development of these theories. There are also more elaborate theories which in

some ways account better for the experimental results obtained and the subject has been critically reviewed at some length[9].

All of these theories show that the concentration of molecules sufficiently active to decompose is not maintained at its equilibrium value at low pressures and that the rate of reaction therefore falls off as the concentration of reactant is lowered; the order of reaction changes from being first order at high pressures to being second order at low pressures. There are several reactions which show this type of behaviour and they have been used to verify the theories[9].

These theories predict that the addition of an inert gas should activate reactant molecules by collision. Thus an inert gas should be capable of increasing the rate of reaction under conditions where the rate has fallen below its maximum high pressure value. This has also been proved experimentally and it is possible to derive "efficiencies" of these inert gases in transferring energy to the reactant molecules relative to the efficiency of the reactant itself[9]. On this basis, the efficiency of a given inert gas naturally varies from reaction to reaction, but, as a general rule, the more complicated molecules are more efficient in transferring energy. Although the efficiency of a gas varies from reaction to reaction, the limits of variation are usually within a factor of 10. In the present investigation, inert gas efficiencies much lower than had been found by other workers were produced, and it was this which first made it seem unlikely that a change which had been found in the order of reaction

was wholly due to the Hinshelwood-Lindemann effect.

For the sake of completeness, there is given in appendix (i) the formal Lindemann mechanism and the method devised by Johnston[40] which was used in this work to calculate inert gas efficiencies.

In 1928, Polanyi and Wigner[71] reviewed the reactions then considered to be unimolecular and found that in the Arrhenius equation

$$k = A e^{-E/RT}$$

that the frequency factor A was of the order of 10^{13} $secs^{-1}$. This value of 10^{13} $secs^{-1}$ is of the order of vibrational frequency of most bonds and they suggested that A factors for unimolecular reactions should be of the order of 10^{13} $secs^{-1}$. None of the reactions cited by them is now considered to be a genuine unimolecular decomposition but most reactions now thought to be truly unimolecular do have A factors of between 10^{11} and 10^{15}. There are cases, however, where it is as low as 10^{8} and reactions are reported with A as high as 10^{18}. Steacie[8] considers that many values of $A = 10^{13}$ have not been found by a truly objective plot of the data, but nevertheless, A factors between $10^{11.5}$ and $10^{14.5}$ are regarded as "normal".

Bond Dissociation Energies.

Chemical bonds are made and broken in chemical reactions. From a knowledge of the strengths of bonds, it might be possible to decide which mechanism a reaction would follow and how fast it might proceed. It has been found that the strength of a given type of bond varies from

compound to compound, and interesting relationships have been found among bond dissociation energy, bond length and molecular environment.

The most common measure of bond strength is the bond dissociation energy. The bond dissociation energy, D (X - Y) of a bond X - Y is defined as the change in energy at absolute zero in the ideal gas state, ΔE_0° for the reaction

$$XY \longrightarrow X + Y$$

the products being in their ground states.

Methods of Determining Bond Energies.

1) Calorimetric Methods

If the heat absorbed when dissociation of a bond took place could be measured, this would give directly the bond dissociation energy of the bond being broken. This has not so far been done, but the heat of recombination of atoms or radicals has been measured in a few cases. D (H-H) has been measured in this way as 105 ± 5.5[72].

2) Thermal Methods

a) Equilibrium Methods

This depends upon the production of the stable equilibrium

$$AB \rightleftharpoons A + B$$

at various temperatures and the determination of the equilibrium constants. It has been done for several diatomic molecules but is difficult to apply where free radicals are produced as these will probably react further.

b) Kinetic Methods

In this method, the activation energy for the process

$$X\,Y \longrightarrow X + Y$$

is found by measuring the rate at different temperatures. It is assumed that there is no activation energy for the recombination

$$X + Y \longrightarrow X\,Y$$

and that the activation energy = Δ H.

In theory, it should be possible to determine the concentrations of X, Y and XY by use of a mass spectrometer but there are considerable technical difficulties in this method. The method was first used by Eltenton[75] and has also been used by Lossing[74].

When the mass spectrometer is not used to determine radical concentrations directly, several conditions have to be fulfilled in order to allow D (X-Y) to be determined:-

(i) The rate determining step should be the breaking of the bond being examined.

(ii) The mechanism should be known.

(iii) There should be no side reactions or their extent should be accurately assessed.

Attempts have been made to produce clean, well-defined reactions by making the initially formed radicals react with metallic mirrors as used by Rice[41] or by using toluene to react with the radicals in the technique developed by Szwarc[75]. This "toluene carrier" technique depends on the stability of the benzyl radical and the low $C_6H_5CH_2$-H bond energy in toluene. The initially formed radicals react with

toluene and produce benzyl radicals which eventually dimerise to dibenzyl:-

$$R + C_6H_5CH_3 \longrightarrow RH + C_6H_5CH_2$$

$$2\ C_6H_5CH_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

If all the initially formed radicals do react in this way, the kinetics of decomposition are greatly simplified for no back reaction or chain reaction can occur.

Butler and Polanyi attempted to measure bond dissociation energies of iodides by working with a fast flow system at low pressure as described in the review of iodide decompositions. Their assumptions about stopping secondary reactions are not valid and their work gives only a rough idea of the variations in D (C-I).

If a full kinetic investigation of a reaction is carried out, and the mechanism completely elucidated, it is possible to determine bond energies from the rate constants for individual steps. This has been done for the bromination of methane[76] .

5) Spectroscopic Methods

The complete interpretation of the U.V. spectrum of molecules allows bond energies to be found. Unfortunately, the spectra are complicated and the interpretations difficult with the result that the method has so far been applied to diatomic molecules only. When it can be used, the method gives very accurate results.

It is also possible to use photodecomposition, but this method gives only an upper limit.

4) Electron Impact Methods

In this method, the energy of the process

$$AB + e \longrightarrow A^+ + B + 2e \text{ - - - - - - - - - - - - - a}$$

is measured. If the energy for the process

$$A + e \longrightarrow A^+ + 2e \text{ - - - - - - - - - - - - - - - - - b}$$

is known, the bond energy D (A-B) may be found by use of the equation

$$A(A^+) = D(A\text{-}B) + I(A) + \text{k.e.} + \text{e.e.}$$

where $A(A^+)$ = appearance potential of A^+ (Reaction a)

$I(A)$ = Ionisation potential of A (Reaction b)

k.e. = kinetic energy of fragments

e.e. = excitation energy of fragments.

This method has been used to determine D (CF_3-I), and the wide spread of values indicate the difficulty of interpreting the data. The results for CF_3I are discussed below.

5) From Other Results.

If Δ Hf of A-B, Δ Hf of A and D (A-B) are known, ΔHf of B may be calculated. The bond energy D (B-C) may then be calculated for any compound BC for which Δ Hf is known. The method often provides a useful cross-check.

6) From Calculation.

It should be possible by quantum mechanical calculations to evaluate D (A-B). So far, this has been done for H_2^+ but no solution has yet been found for more complicated molecules.

Previous Determinations of D (CF_3-I)

Several attempts have been made to evaluate D (CF_3-I) by electron impact methods. The principle of the method, as outlined earlier, is to measure the appearance potential of some fragment, and by subtracting the ionisation potential of the fragment from its appearance potential, the energy of the bond linking the fragment to the rest of the molecule may be obtained. Allowance must also be made for any excess energy. To obtain a value for D (CF_3-I), it is therefore necessary to find A (CF_3^+) and I (CF_3) or to find A (I^+) and I (I).

a) D (CF_3-I) from A (CF_3^+) and I (CF_3)

The measurement of A (CF_3^+) is fairly straightforward but evaluation of I (CF_3) presents some difficulty. Two methods have been used to obtain I (CF_3).

(i) Farmer, Henderson, Lossing and Marsden[60] measured I (CF_3) directly by producing CF_3 radicals in the pyrolysis of CF_3-N=N-CF_3. They obtained a value of I (CF_3) = 10.10 e.v. which, when combined with their unquoted A (CF_3^+) lead to a value of D (CF_3 -I) which was "too low by an amount approaching 1 e.v.". They also obtained anomalous results with CF_3Cl and CF_3Br.

However, from CF_3H, values of D (CF_3-H) = 102 $\pm$ 2 K cals/mole and hence Δ Hf (CF_3) = -118 $\pm$ 2 K cals/mole were obtained, and from CF_4 a value of D (CF_3-F) = 125 $\pm$ 2 K cals/mole was derived

which gives Δ Hf (CF_3) = -115 ± 2 K cals/mole. These values are in agreement with D (CF_3-H) = 102.0 ± 2 K cals/mole[63] and D (CF_3-F) = 116.5 K cals/mole[53]. From their mean value of Δ Hf (CF_3) = -117 ± 2 K cals/mole and Δ Hf (CF_3Cl) = 171 ± 1 K cals/mole,[77] a value of D (CF_3-Cl) = 83 ± 5 K cals/mole is obtained which is in fair agreement with D (CF_3-Cl) = 79.5 ± 2 K cals/mole[53]. No values of Δ Hf (CF_3Br) or Δ Hf (CF_3I) are available. This value of I (CF_3) = 10.10 e.v. does give some reasonable results.

(ii) The other method of obtaining I (CF_3) is to measure A (CF_3^+) from a compound CF_3X where D (CF_3-X) is known. I (CF_3) may then be calculated by use of the energy equation

$$A(CF_3^+) = D(CF_3\text{-}X) + I(CF_3) + k.e. + e.e.$$

The value D (CF_3-Cl) = 79.5 ± 2 K cals/mole has been obtained from sodium flame experiments[53] and D (CF_3-Br) = 64.5 K cals/mole has been found by the toluene carrier technique[51]. Dibeler, Reese and Mohler[78] have used this method to obtain I (CF_3) = 9.5 ± 0.2 e.v. and Marriott and Craggs[79] derive I (CF_3) $\leqslant$ 9.35 e.v. Neither set of workers used the value D (CF_3-F) = 116.5 K cals/mole[53] but Dibeler, Reese and Mohler use their data to support a value of D (CF_3-F) = 145 ± 5 K cals/mole in agreement with 158 ± 4 derived by Luft[80]. From A (CF_3^+) in CF_3I = 11.28 ± .02 e.v., Marriott and Craggs obtain D (CF_3-I) = 1.9 e.v. = 43.7 K cals/mole, and Dibeler, Reese and Mohler who found A (CF_3^+) in CF_3I = 11.4 ± 0.4 e.v., derive D (CF_3-I) = 2.1 ± 0.2 = 48.5 ± 5 K cals/mole. Experiments were

carried out by these workers which show that the CF_3^+ ions have no excess energy and are not formed by an ion pair process.

There are also in the literature two other values of I (CF_3) by Dibeler Reese and Mohler[81] of 8.9 e.v. and 8.5 e.v. but these they regard as incorrect because of an invalid assumption that the excess energy would be the same for the two types of process

$$XY + \epsilon \longrightarrow X^+ + Y + 2\epsilon + \text{excess energy.}$$

$$XY + \epsilon \longrightarrow X + Y^+ + 2\epsilon + \text{excess energy.}$$

b) D (CF_3-I) from A (I^+) and I (I)

The value of I (I) is known from spectroscopic work to be 10.44 e.v.[82]. Farmer et alia measured A (I) from CF_3I = 12.9 ± .15 e.v. and obtained from this D (CF_3-I) = 2.46 ± .15 e.v. or 57 ± 4 K cals/mole.

Marriott and Craggs obtained three values of A (I^+) from CF_3I; the value which they attributed to the process:-

$$CF_3I + \epsilon \longrightarrow CF_3 + I^+ + 2\epsilon + \text{k.e.} + \text{e.e.}$$

is 13.25 ± .07 e.v., 0.9 e.v. of this being due to excess energy.

Dibeler Reese and Mohler give A (I^+) = 13.6 e.v. which they identify with the ion pair process:-

$$CF_3I + \epsilon \longrightarrow CF_2 + I^+ + F^- + \epsilon + \text{k.e.}$$

where k.e. is about 0.4 e.v.

There would thus appear to be some confusion about the value of D (CF_3-I), the spread of values being between 45.7 and 61 K cals/mole at worst. The results of this electron impact work, together with

TABLE 1

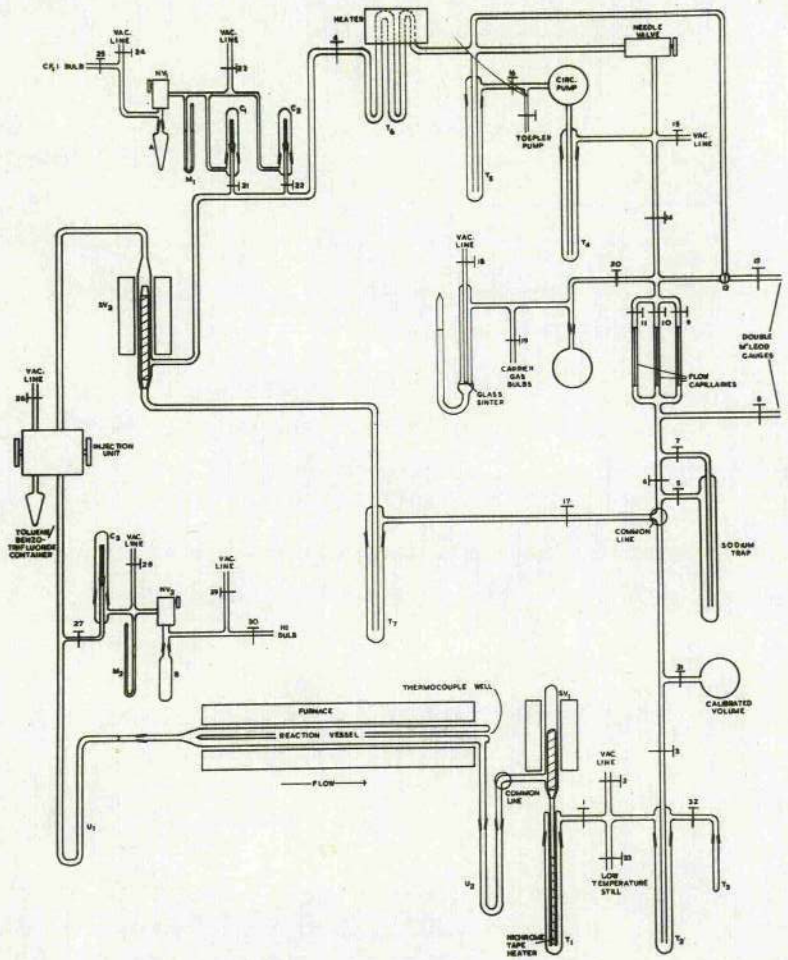
Electron Impact Data.

		Appearance Potential Measurements (e.v.)				
Reference		81	83	60	79	84
Compound	Ion					
CF_3H	CF_3^+			$14.53\pm.05$		
CF_4	CF_3^+	16.0 ± 0.2	$15.44\pm.05$	$15.44\pm.05$ used.		
CF_3Cl	CF_3^+	12.7 ± 0.2	$12.95\pm.05$	$13.06\pm.06$		
CF_3Br	CF_3^+	12.5 ± 0.5		12.1	12.15 ± 0.02	12.51 ± 0.05
CF_3I	CF_3^+	11.4 ± 0.4			11.28 ± 0.02	
	I^+	13.6 ± 0.5		12.9 ± 0.15	13.25 ± 0.07	
I (CF_3) direct				10.10 ± 0.05		
I (CF_3) indirect		9.3 ± 0.2			<9.55	
Derived Quantities (K cals/mole)						
Δ Hf (CF_3)				-117 ± 2		
D (CF_3-H)				102 ± 2		
D (CF_3-F)		145 ± 5		125 ± 2		
D (CF_3-Cl)				83 ± 3		
D (CF_3-I)		48.5 ± 5		57 ± 4	43.7	

some relevant data by Warren and Craggs[83] and Jacobson, Steigman, Strakna and Friedland[84] is given in table 1.

FIGURE 1

FLOW SYSTEM



THE PRESENT INVESTIGATION.

Apparatus and Experimental Technique.

Two distinct types of experiment were carried out

(i) Low pressure experiments in a flow system with up to 16 mms. of different gases.

(ii) Higher pressure experiments in sealed bulbs with up to 700 mms. of various reactants.

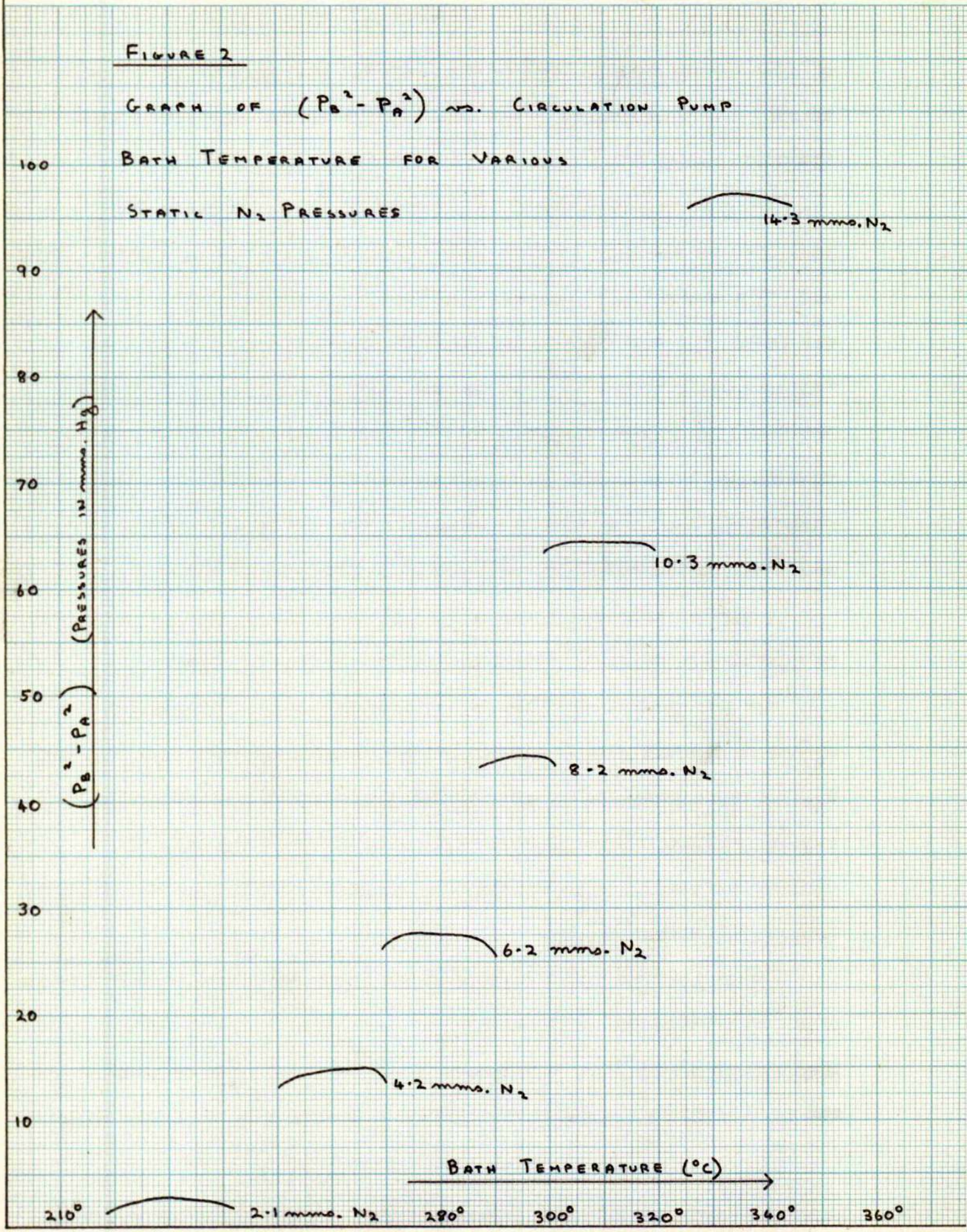
The following is a description of the flow system apparatus and the general technique used; any special modification is described later in the appropriate section. Figure 1 is a diagram of the complete apparatus.

The Vacuum Line. The apparatus was evacuated by means of a single stage mercury diffusion pump backed by an Edwards Speedivac rotary oil pump. A pressure of 10^{-5} mms. of mercury could normally be obtained in the whole apparatus, the pressure being read on a single McLeod gauge.

The Circulating Pump. The gas was circulated by means of a mercury diffusion pump with three jets in parallel, the boiler of which was heated by a solder bath. This bath was maintained within one degree of a fixed temperature by means of a Sunvic energy regulator (type TYB 1); the stem of the pump was heated electrically by means of nichrome tape wound directly on the stem and was lagged to prevent heat loss. It has been demonstrated by Moore[85] that the efficiency

FIGURE 2

GRAPH OF $(P_B^2 - P_A^2)$ vs. CIRCULATION PUMP BATH TEMPERATURE FOR VARIOUS STATIC N_2 PRESSURES



of such a pump depends both on the bath temperature and the pressure of gas, and by Alexander[86] that the heating of the stem influences the performance.

The pump was calibrated by plotting $(p_B^2-p_A^2)$ which is proportional to the rate of flow (where p_B and p_A are the pressures before and after a capillary) against the bath temperature (figure 2). It was found that for a given gas pressure that over a range of bath temperature of some 20C° that the rate of pumping remained constant; above and below this temperature, the rate decreased. The optimum temperature varied with gas pressure as shown in figure 2. During an experiment, the bath temperature was kept in the middle of the required temperature range thus ensuring constancy of flow.

A needle valve was provided as a by pass to the pump; adjustment of this needle valve allowed fine control of the gas flow.

The gas entered the pump after passing through a liquid air trap T_4 and on leaving passed through another liquid air trap T_5. In trap T_6, the gas stream was alternately heated to 300°C and cooled to liquid air temperature to remove colloidal mercury fog from the circulation pump; this arrangement prevented mercury vapour distilling through the apparatus.

Before entering the reaction vessel, the gas stream passed through a jet to prevent back diffusion.

Measurement of Gas Flow and Pressure. The rate of flow of carrier gas was determined by measuring the pressure on each side of a capillary

CAPILLARY CALIBRATION APPARATUS

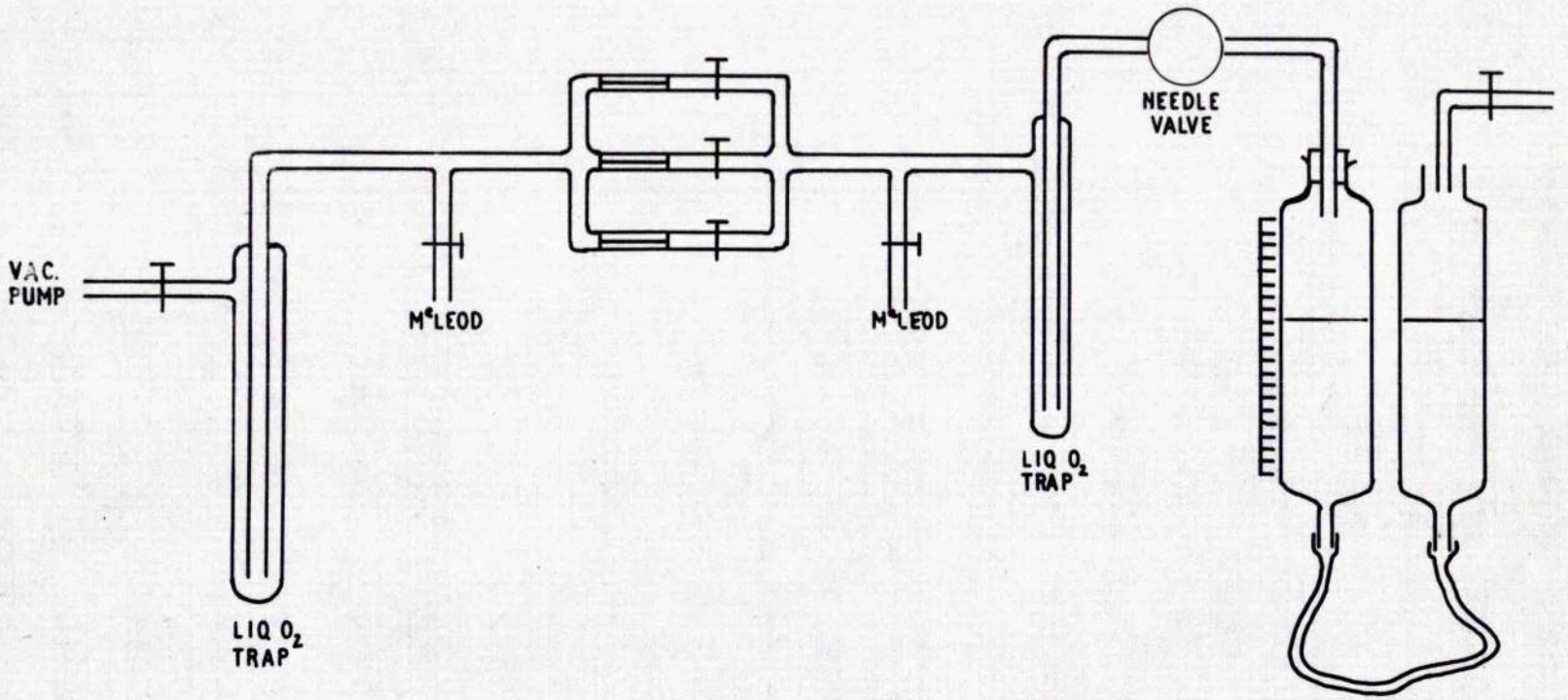


FIGURE 3

by means of double McLeod gauges. In theory, the rate of flow of gas through a capillary of known dimensions should be calculable by means of Meyers modification of Poiseuille's Law. The number of moles of gas flowing per second is given by

$$n = \frac{\pi r^4 (p_B^2 - p_A^2)}{16 \, l \, R \, T \, \eta}$$

where n = gas flow in moles/sec.

r = radius of capillary in cms.

p_B = pressure before the capillary in dynes/cm^2.

p_A = pressure after the capillary in dynes/cm^2.

l = length of capillary in cms.

R = the gas constant.

T = absolute temperature.

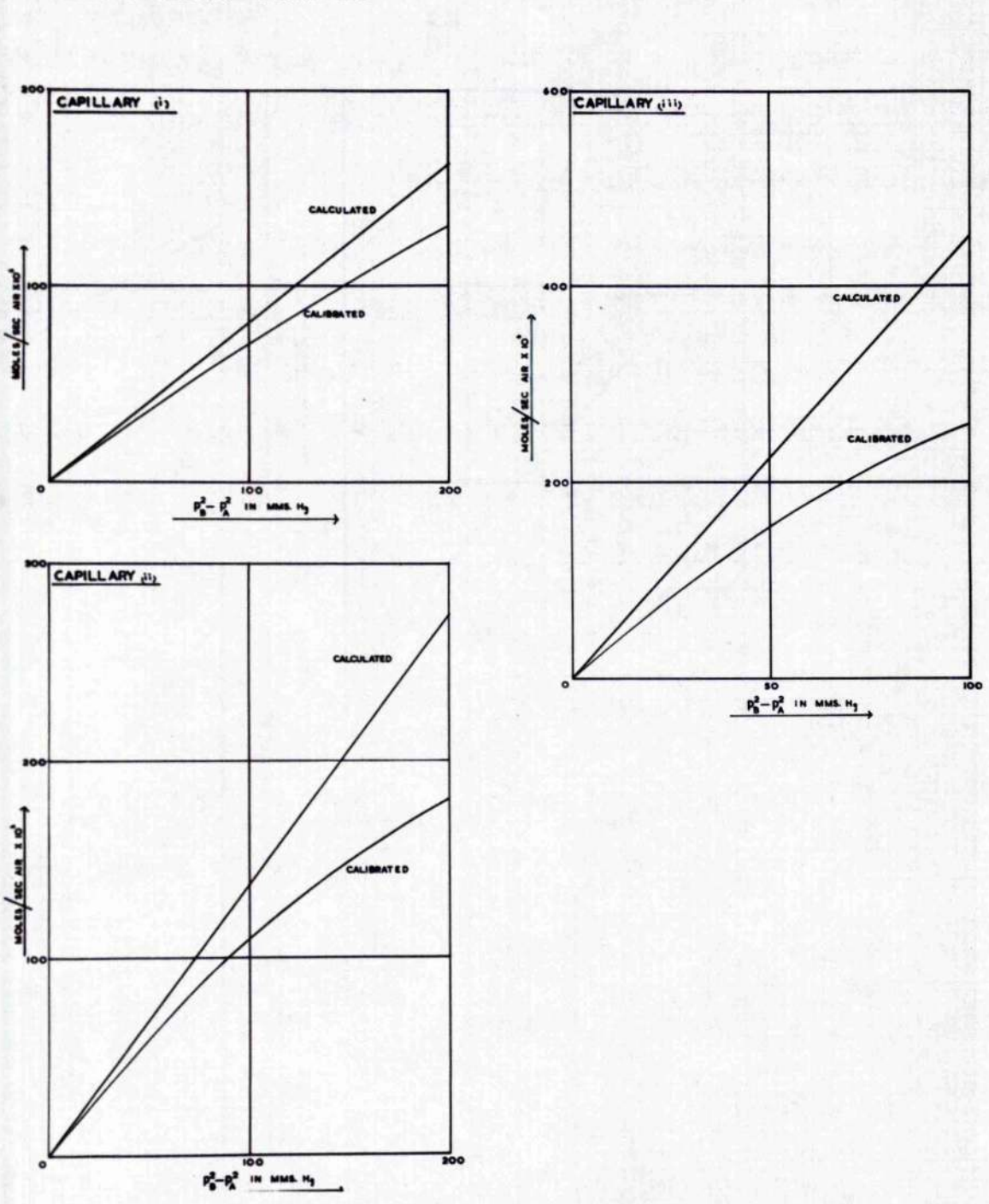
η = viscosity in poise.

This may be written $n = k(p_B^2 - p_A^2)$

where $k = \frac{\pi r^4}{16 \, l \, R \, T \, \eta}$

It has been found by previous workers[2,5,86] that at low pressures, with capillaries of the dimensions used here, that deviations from theoretical behaviour occurred and that it was best to calibrate the capillaries in situ. The method of calibrating involved the pumping through the capillary, at a steady rate, a measured amount of dry air in a measured time; the experimental arrangement is shown in figure 3. A needle valve was placed between the air reservoir and the flow

FIGURE 4


FLOW CAPILLARY DEVIATIONS
FIGURE 4
CAPILLARY (i)
CALCULATED
CALIBRATED
MOLES/SEC. AIR X 10⁴
200
100
0
100
200
$P_B^2 - P_A^2$ IN MMS. H_2
CAPILLARY (ii)
CALCULATED
CALIBRATED
MOLES/SEC. AIR X 10⁴
300
200
100
0
100
200
$P_B^2 - P_A^2$ IN MMS. H_2
CAPILLARY (iii)
CALCULATED
CALIBRATED
MOLES/SEC. AIR X 10⁴
600
400
200
0
50
100
$P_B^2 - P_A^2$ IN MMS. H_2

capillary and this allowed pressures similar to those of actual experiments to be maintained across the capillary.

It was found that at low rates of flow, the rate of flow of gas was as calculated, but at higher rates the flow fell below that calculated from $n = k (p_B^2 - p_A^2)$. The deviations from ideal behaviour occurred at lower values of $(p_B^2 - p_A^2)$ as the length of the capillary was decreased and the bore increased. The observed calibrations for air were corrected for the viscosities of the gases used, the values being those given by Partington[87].

The dimensions and calculated constants of the three capillaries used are given in table 2 and the deviations from the calculated rates of flow are illustrated in figure 4.

TABLE 2

Flow Capillaries.

Capillary	Length (cms)	Radius (cms)	Capillary Constant (Pressure in mms.Hg) Moles air/sec $\times 10^6$
(i)	14.30	.1095	0.813
(ii)	7.975	.1081	1.580
(iii)	5.150	.1299	4.469

In order to determine the contact time it is necessary to know the average pressure in the reaction vessel. This was found by use of

the empirical equation

$$P_F = P_B + Z\,(P_c - P_B)$$

where P_F = average pressure in reaction vessel

P_B = pressure before capillary

P_C = pressure between traps T_5 and T_6 at circulating pump.

The value of the factor Z was found by experiment for the conditions used. The reaction vessel was connected via a trap cooled in liquid air to the McLeod gauge which was also used to measure p_B. Under steady flow conditions (and steady rate of injection of toluene in some cases), the values of p_F p_B and p_C were found. This allowed a value of Z to be calculated. The values of Z ranged from 0.15 where both the metal valve and HI injection system were in position to 0.45 where only CF_3I could be introduced to the gas flow. A two way tap was normally used on one McLeod so that either p_A or p_C could be measured; the other McLeod was used to read p_B only, the lead to the furnace being sealed off.

The Reaction Vessels. Three reaction vessels were used in the flow experiments. For the experiments where CF_3I was decomposed alone and for initial experiments with toluene, a nickel vessel was used for the reasons already stated. This vessel was 92 cms. long; the central part of 45 cms. length was 2.9 cms. in diameter and this tapered down at each end to a 22 cm. length of 1.5 cms. diameter tube. The tube was drawn to these specifications by H. Wiggin and Co. A nickel tube to accommodate a glass thermocouple well was silver soldered to the

outside of the large diameter part; three thermocouples were also attached at intervals to each narrow tube to examine the rate of fall off of temperature. A temperature uniform to $\pm$0.5 C degrees could be obtained over the central 45 cm. portion and the temperature fall off along the narrow tube was fairly rapid. The reaction volume was 290 mls.

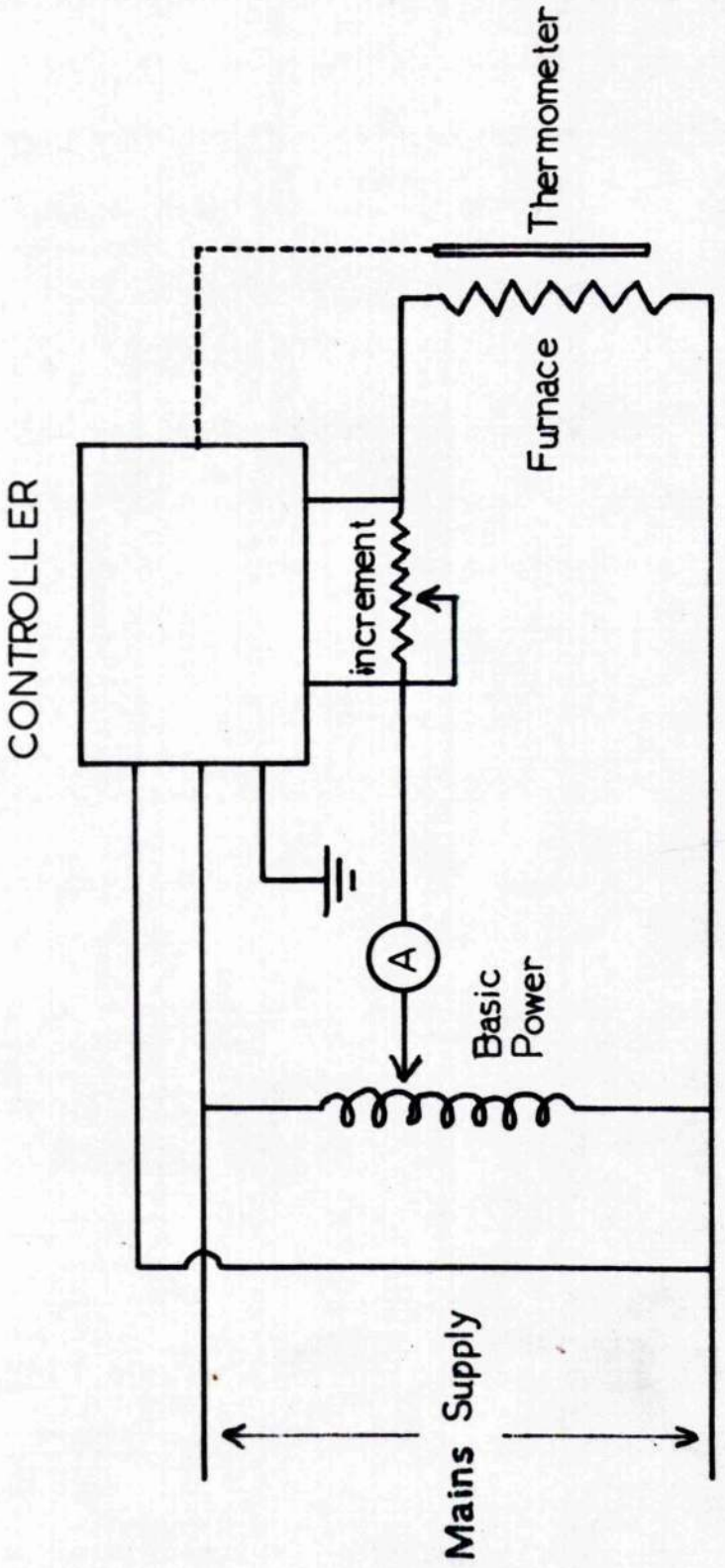
For most of the flow experiments a pyrex glass reaction vessel of volume 214 mls. was used. This vessel was fitted with a central thermocouple well and the temperature was uniform to $\pm$ 1.5 C^{o} along its length.

In the experiments where the effect of surface area was investigated, a pyrex glass reaction vessel was used where the exit end and central thermocouple tube could be removed by means of a ground glass joint; tubes of known dimensions could be inserted to change the surface to volume ratio if desired. The temperature of this vessel was also uniform to $\pm$ 1.5 C^{o} along its length.

The Furnace. The furnace consisted of an inconel tube 60 cms. long and 49 mms. diameter covered with a layer of alundum cement. This was wound with Brightray C heating tape which was covered with another layer of alundum cement and finally lagged with asbestos pipe covering. The winding was closer at the ends of the tube and six tappings were made along it so that shunts could be inserted to obtain a uniform temperature along the length of a reaction vessel.

Temperature Control and Measurement. The temperature was controlled

FIGURE 5


Thermometer
Furnace
CONTROLLER
increment
A
Basic Power
Mains Supply

by means of a furnace controller which used a circuit similar to that of the Sunvic RT2 controller. The temperature sensitive element consisted of a platinum resistance thermometer and the controller functioned by intermittently shorting out a resistance in series with the furnace winding. The arrangement is shown in figure 5.

The temperature was measured by means of a chromel alumel thermocouple. The e.m.f. was read on a direct reading Gambrell potentiometer, the calibration of Rosser, Dahl and Gowens[88] being used to find the temperature. The thermocouple was checked against a newly made thermocouple and found to agree with it to within $\pm$ 0.5 C^{o}, and couples made from the same coils of wire had been shown previously to agree with fixed point calibrations at the melting points of ice, tin, lead, zinc and silver and the boiling points of sulphur and water.

Collection of the Products. Three product collection traps in parallel were used, a fourth trap was also used when trying to obtain steady conditions at the start of an experiment. After leaving the reaction vessel, the gas stream passed through a U tube, U_2, into one of four possible paths (only one is illustrated in the diagram) controlled by four all glass valves (SV_1). An all glass valve consisted of a plunger with a piece of soft iron sealed into it; the bottom of the plunger was ground and fitted into a ground seat. The plungers were raised and lowered by means of solenoids the currents through which were controlled by a sliding resistor; each solenoid could be switched on or off independently of the others.

The gas stream then passed down a double walled tube with a nichrome tape heater wound in the interspace. This made the iodine condense out at a suitable place on the wall of the tube and prevented blocking of the tube by less volatile materials. The gas passed through trap T_1, tap 1, trap T_2 and rejoined the common line via tap 3. Trap T_2 was packed with glass wool to assist in the removal of very volatile materials. The system of traps T_2 and T_3 could be evacuated independently via tap 2.

Introduction of Materials to the Flow Line.

Carrier Gases. Nitrogen and argon were measured into the system by means of the manostat controlled by taps 18, 19 and 20. The gas entered the manostat via tap 19 and depressed the mercury until it reached the level of the sinter connected via tap 18 to the vacuum line. Tap 19 was then shut and the fixed amount of gas enclosed in the manostat was admitted to the flow line by opening tap 20.

Injection of CF_3I. The CF_3I was injected into the carrier gas stream by means of the apparatus shown in figure 1. It was stored in a 5 l. black painted bulb and the injection system could be evacuated by taps 23 and 24. The CF_3I entered the gas stream through one or both of the capillaries in the interchangeable capillary holders C_1 and C_2 connected to the flow line by taps 21 and 22. In use, the reservoir A was immersed in liquid air and some CF_3I frozen into it from the 5 l. bulb. The liquid air was then replaced by a -78°C bath at which temperature CF_3I has a vapour pressure of 54 mms. In

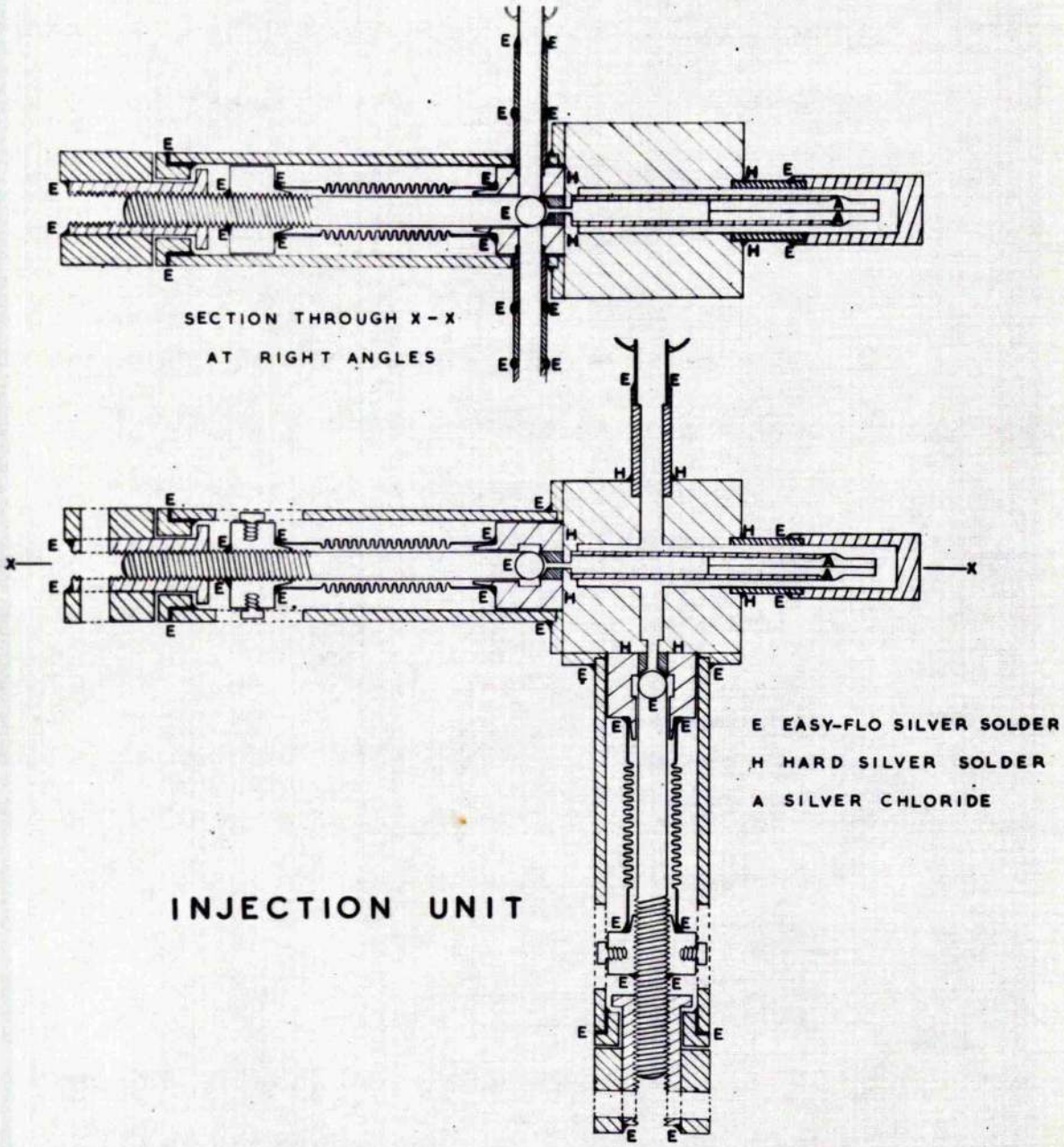
order to obtain steady injection, the pressure before the injection capillaries, as read on manometer M_1, and controlled by needle valve NV_1, was always kept above 25 mms. by changing the capillaries.

In order to assess the amount of CF_3I passed in an experiment, the rate of injection was measured by raising the two way solenoid valve SV_2 and diverting the gas stream through T_7 where the CF_3I was frozen out in liquid air. After pumping away the carrier gas, the CF_3I was distilled into a calibrated volume to which was attached a manometer. Tap 31 was then closed and the pressure, volume and temperature of the CF_3I measured. This allowed the injection rate to be calculated. By injecting CF_3I with the furnace cold, it was found that the delivery into the three product collection traps and T_7 was constant to within $\pm$ 2 % at worst.

Injection of Toluene. Only above 20°C does toluene attain a vapour pressure sufficiently high for its steady injection through a capillary into a gas stream at the pressures used here. Thus any system for its injection will have to be heated to at least this temperature. This makes the use of grease lubricated taps difficult and there is the additional complication that toluene dissolves in tap grease. An all metal valve injection unit illustrated in figure 6 was therefore constructed which was joined to the toluene container and the rest of the system by means of metal to glass seals; this arrangement can be heated to about 150°C if required.

The body of the valve was constructed of mild steel. The valve

FIGURE 6



INJECTION UNIT

could be closed, opened or evacuated by screwing down the appropriate copper tipped silver steel rods on to stainless steel valve seats. The silver steel rods were connected to the valve body by means of Drayton flexible brass bellows. The ends of the rods outside the bellows were threaded and the rod actuated by a nut screwed on to the rod and held captive on a steel tube bolted to the valve body. (The nut could only be rotated and could not move up and down relative to the steel tube). Rotation of the bellows was prevented by two 6.B.A. guide screws which moved in slots milled in this steel tube. The injection capillary consisted of a drawn piece of glass tubing fixed into the stainless steel capillary holder with silver chloride cement. A removable cap allowed the capillary to be interchanged if required. All the joints on the valve were soldered with silver alloys so that the bellows could be removed without impairing the sealing of the other joints. Nichrome tape heaters were wound on the steel tubes surrounding the bellows and around the body of the valve. The valve was tested for leaks on the mass spectrometer.

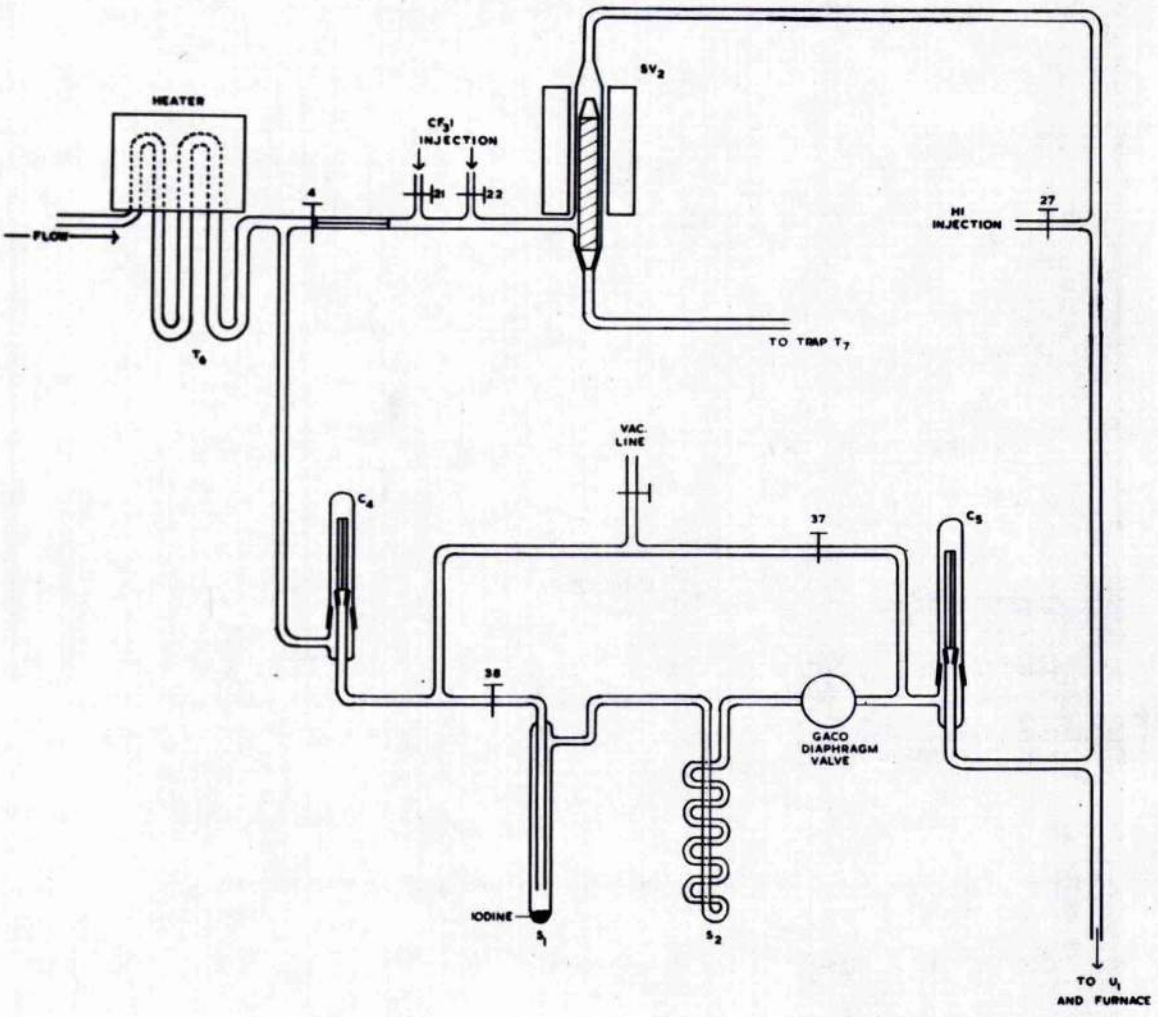
The toluene reservoir was immersed in a small stirred, water filled thermostat bath fitted with a nichrome tape heater. The current through the heater was switched on and off by a Sunvic bimetallic stem thermostat switch; the temperature could be kept constant to $\pm$ 0.1 C^{o} within the range 20^{o}C to 55^{o}C.

Benzotrifluoride was also injected by the same method.

Injection of HI. Hydrogen iodide was injected by an apparatus similar

FIGURE 7

IODINE INJECTION SYSTEM



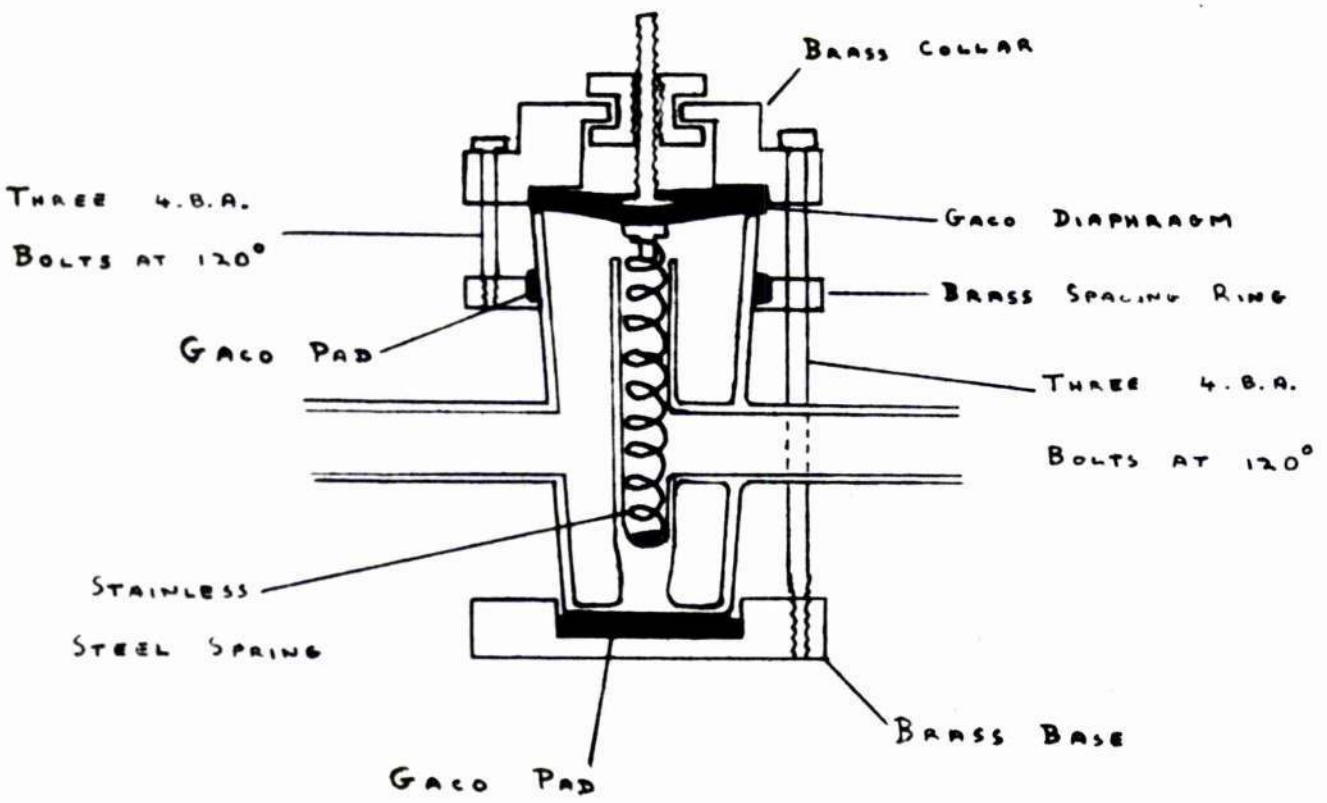
to that used for CF_3I except that only one interchangeable capillary holder C_5 was used. The injection tap 27 led into the flow line between the toluene valve and the furnace inlet. The HI was stored in black painted bulbs beyond tap 30. Operation of the unit was similar to the working of the CF_3I injector. The vacuum taps 28 and 29 and taps 27 and 30 were all lubricated with Edwards Silicone High Vacuum grease and the mercury in manometer M_2 was protected by a 2 cm. depth of silicone pump oil; these silicone products are not attacked by HI.

Injection of Iodine. This is technically difficult, for iodine dissolves in both silicone and ordinary tap greases and reacts with the latter. It attacks most metals at appreciable rates at the temperatures required for injection through a capillary (about 100°C) and an all metal valve system would require to be constructed of nickel and stainless steel with platinum valve seats. It was found that "gaco" rubber which has been used as a diaphragm material in glass bodied valves was embrittled by iodine vapour at 100°C. An attempt to use nickel bodied valves with teflon diaphragms failed because the teflon flowed under heat and pressure and the valve could not be opened.

It was therefore decided to use a split flow saturator technique to inject iodine using a gaco diaphragm valve as a greaseless tap. The split flow was used so that there could be no possibility of CF_3I or HI dissolving in the iodine in the saturator. The toluene

FIGURE 8

GACO DIAPHRAGM VALVE



injection valve was removed and the apparatus modified from trap T_6 to the furnace inlet (figure 7). C_4 and C_5 are interchangeable capillary holders, another capillary could be piciened into the barrel of tap 4. By this means the flow could be adjusted to be of the same order in the two parts of the split flow. Tap 37 controls a by pass round the saturator. In use, S_2 was immersed in a large Dewar vessel filled with water, ice and water, or ice, water and salt and stirred by bubbling compressed air through it. S_1, which contained solid iodine, was kept some 10 C° higher. This two saturator system gave injection of iodine constant to within 2%. When it was desired not to inject iodine, liquid oxygen was placed round S_1 and S_2, tap 38 and the gaco valve were shut and tap 37 was opened. Because of difficulty in opening the valve when evacuated, a stainless steel spring was placed inside the centre tube. (figure 8)

Preparation and Purification of Reactants.

Nitrogen (B.O.C.) from a cylinder was purified from condensables by passing through a liquid air trap, then through two sodium traps heated to 300°C to remove oxygen and finally through a plug of glass wool to remove sodium oxide. It was stored in a 10 l. bulb. The arrangement is shown in figure 9.

Argon (B.O.C.) was similarly obtained and purified.

Trifluoromethyl Iodide. CF_3I was prepared in a Hunsdiecker reaction by reacting CF_3COOAg with solid I_2 [89, 90, 91].

PURIFICATION OF CARRIER GASES

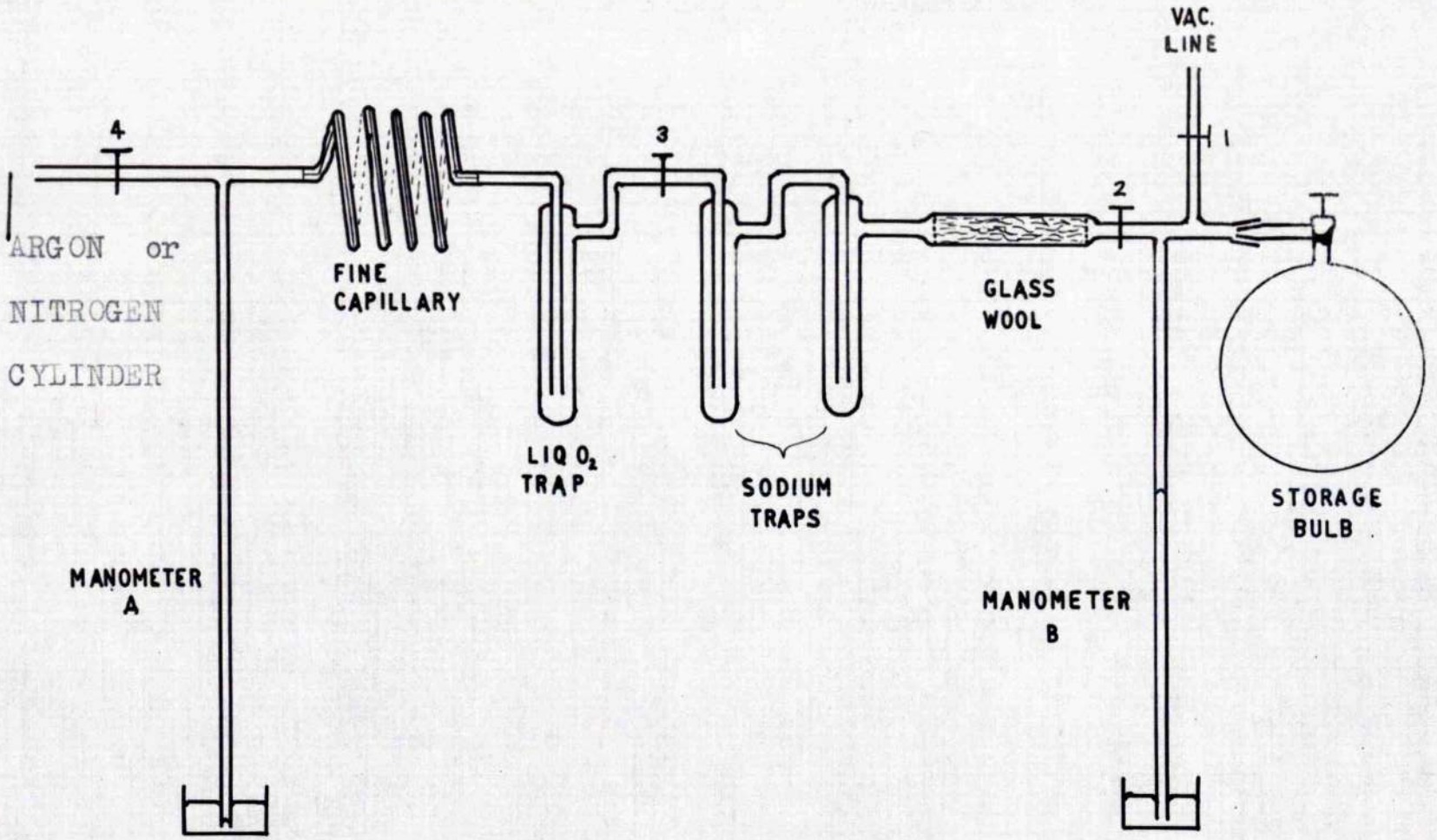


FIGURE 9

$$CF_3COOAg + I_2 \longrightarrow CF_3I + CO_2 + AgI.$$

Trifluoroacetic acid (Minnesota Mining and Manufacturing Co. Ltd., or Eastman Kodak) was distilled through a long Fenske column, the fraction boiling at 72.2 to 72.5°C being collected. Its purity was checked by freezing point and equivalent weight determinations. A 50% aqueous solution of this acid was allowed to react with a slight excess of silver carbonate; the excess carbonate and some precipitated silver oxide were then filtered off. The water was evaporated from the aqueous solution of CF_3COOAg at about 15 mms. pressure from a steam bath and the solid CF_3COOAg was dried on the high vacuum system. This gave a white crystalline solid which was stored in a brown glass desiccator over P_2O_5.

This silver trifluoroacetate was reacted with iodine in the apparatus illustrated in figure 10a. Solid CF_3COOAg and about three times its weight of resublimed iodine (Whiffen) were ground together and the mixture was placed in the one inch diameter nickel tube. The U tube and trap Ta were cooled in ice and salt; the purpose of these, the water cooling coil and the water condenser was to remove iodine. Traps Tb and Tc were cooled to -78°C, tap a was open, taps b and h were shut and the stopper S was removed. The nickel tube was gently warmed with a free flame and a pink gas stream passed into the U tube and traps. Dry nitrogen was passed through the apparatus occasionally to sweep the gas along. Most of the iodine was stopped in the U tube or trap Ta, the CF_3I collected in Tb and Tc as a pink liquid (due to

FIGURES 10a and 10b

FIGURE 10a

CF_3I PREPARATION APPARATUS

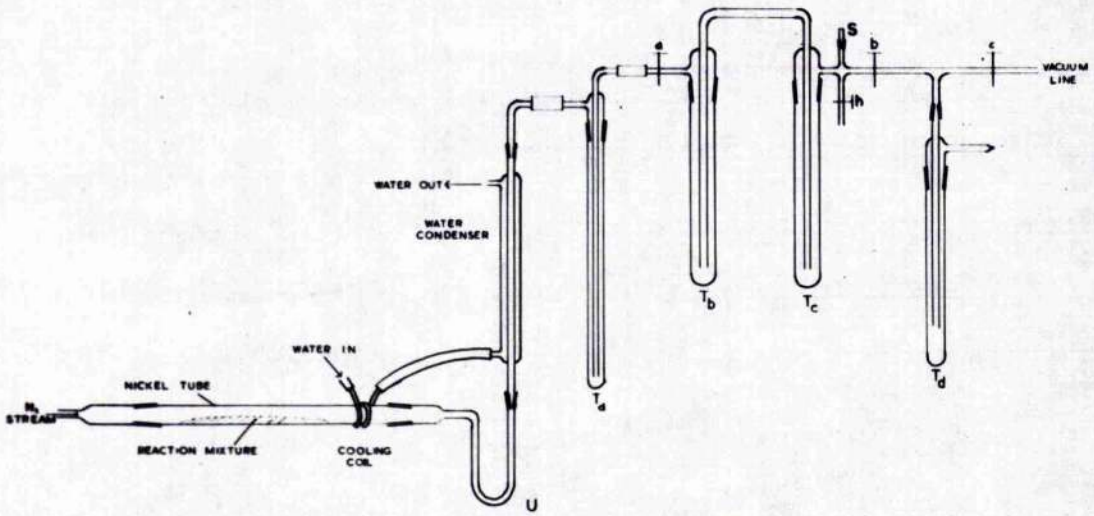
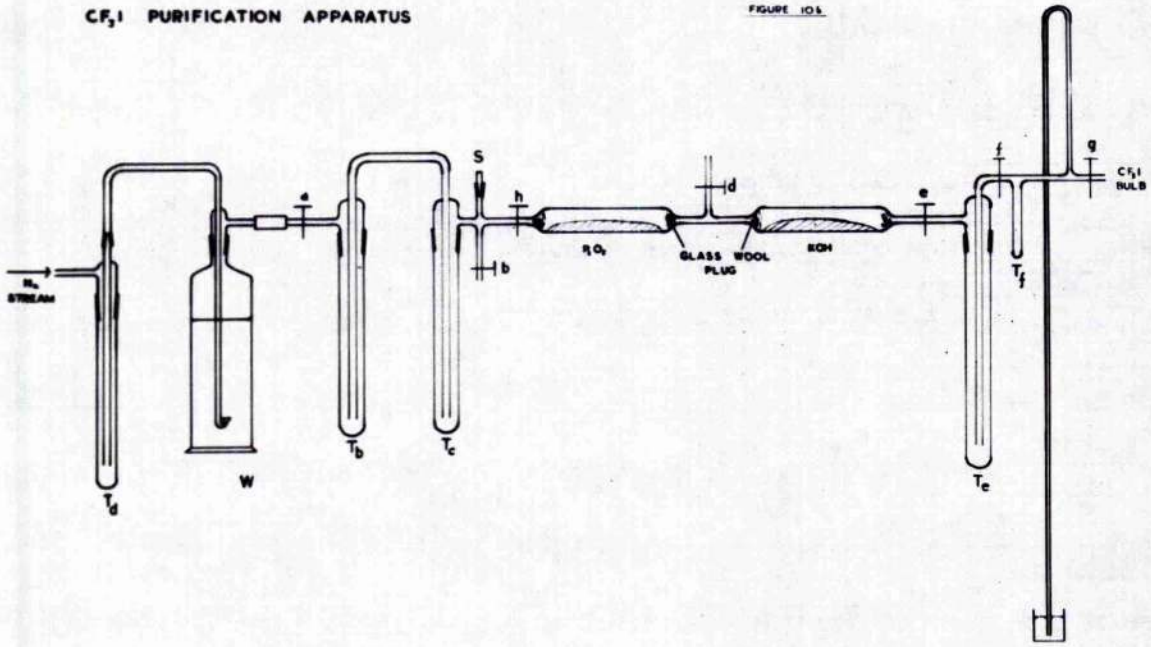


FIGURE 10b

CF_3I PURIFICATION APPARATUS



dissolved iodine) and most of the CO_2 passed through.

When the reaction was completed, tap a was shut and the stopper S inserted, the CF_3I was cooled to -185°C and the system evacuated through c and b. Tap C was then shut and the CF_3I was distilled from Tb and Tc cooled to -78° to trap Td cooled to -185°C. The iodine was retained in Tb and Tc and the CF_3I collected in Td as a white solid.

The CF_3I was then washed with 8% caustic soda solution to remove CO_2, by removing trap Td and attaching it as shown in figure 10b. Nitrogen was used to sweep the CF_3I through the wash bottle W into traps Tb and Tc cooled to -78°C. Tap a was open, taps b and h were shut and S removed. The CF_3I was then cooled to -185°C, tap a shut, S replaced and the system evacuated via taps d and h. This allowed trap to trap distillation in vacuo over P_2O_5 and KOH pellets to remove H_2O, CO_2 and dissolved gases. The CF_3I was allowed to expand from trap Tf beyond tap f and the pressure was read on the manometer; it was stored in black painted bulbs over mercury.

The average yield of a synthesis was about 75% calculated on the trifluoroacetic acid used. The purity was checked on the mass spectrometer. The mass spectrum was completely identifiable with that expected from CF_3I [92] with the addition of small peaks at $\frac{m}{e} = 44^+$ and $\frac{m}{e} = 85^+$. The peak at $\frac{m}{e} = 44^+$ was never more than 0.2% of the parent CF_3I^+ peak and was probably due to CO_2. SiF_4 [93] gives as a major peak SiF_3^+ where $\frac{m}{e} = 85^+$. The 85^+ peak could be reduced

TOLUENE PYROLYSIS APPARATUS

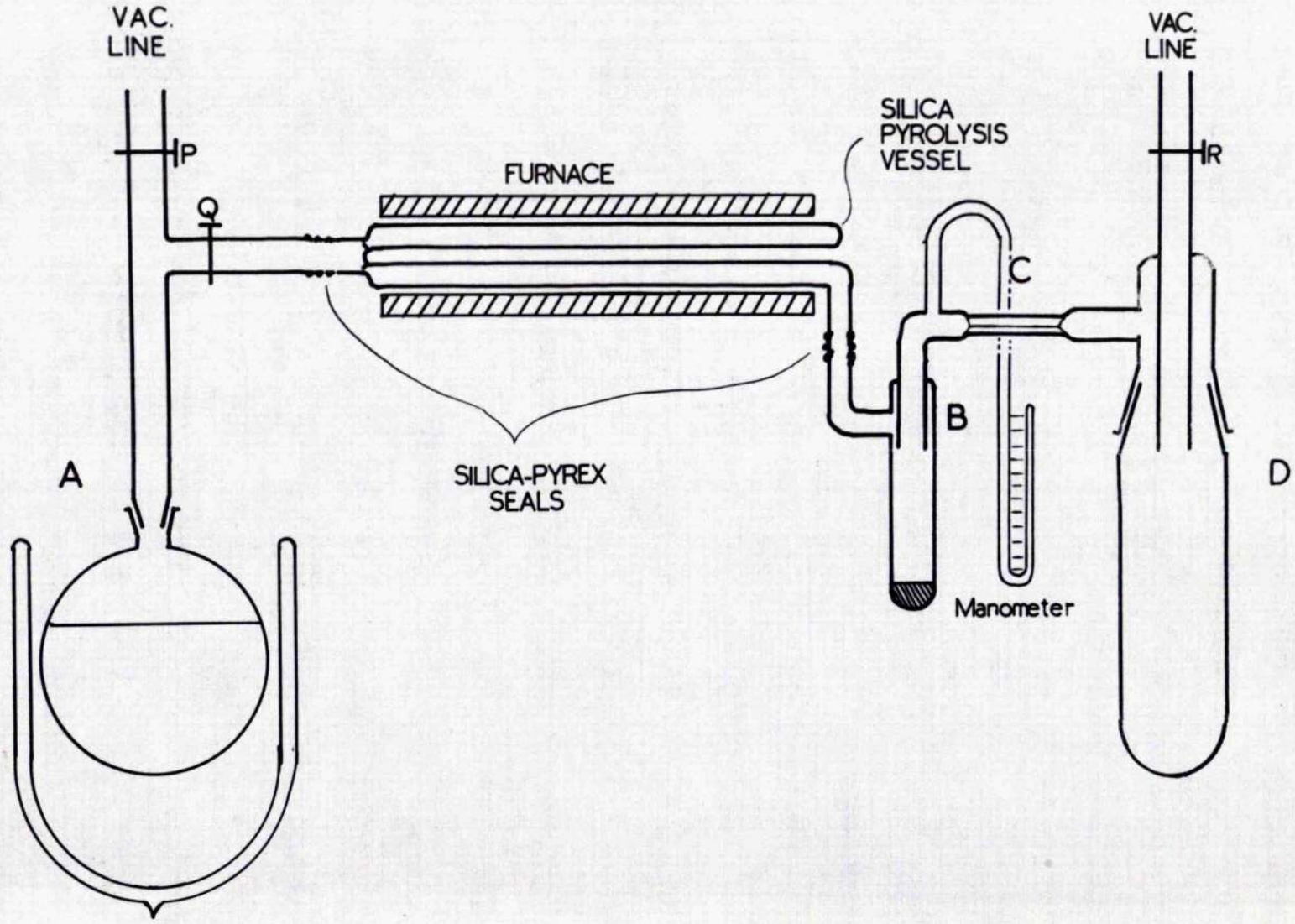


FIGURE 11

by preparing the CF_3I in a nickel tube instead of in pyrex and was also slightly diminished by washing with NaOH but it was never completely eliminated. It was probably due to SiF_4 as impurity and was about 0.3% of the CF_3I^+ peak.

Toluene. For kinetic work, toluene has to be free from impurities which can give active radicals. Szwarc[94] found in his studies on the pyrolysis of toluene that reproducible results could be obtained only from samples of toluene which had previously been partially pyrolysed and distilled. Lapage[2] also found that toluene used as a radical acceptor had to be purified in this way. A simple apparatus was constructed to partially pyrolyse toluene (figure 11). The apparatus was evacuated by taps P and R and the toluene in A degassed by pumping at -80°C. It was then warmed to room temperature and distilled through the silica pyrolysis vessel into traps B and D. Trap B was at room temperature and in it condensed the more involatile products, trap D was kept at -80° and in it was collected impure partially pyrolysed toluene; the gaseous products were continually pumped away via tap R. The furnace was a nichrome wound iron tube similar to the main furnace; it was maintained at about 850°C and the capillary C was such that the contact time was about 0.3 secs.

Reagent grade toluene was shaken with concentrated sulphuric acid, then with sodium carbonate and washed with water. It was dried over $CaCl_2$ and pyrolysed once. The pyrolysis product was again shaken with concentrated sulphuric acid, sodium carbonate and water, dried over

HYDROGEN IODIDE PREPARATION APPARATUS

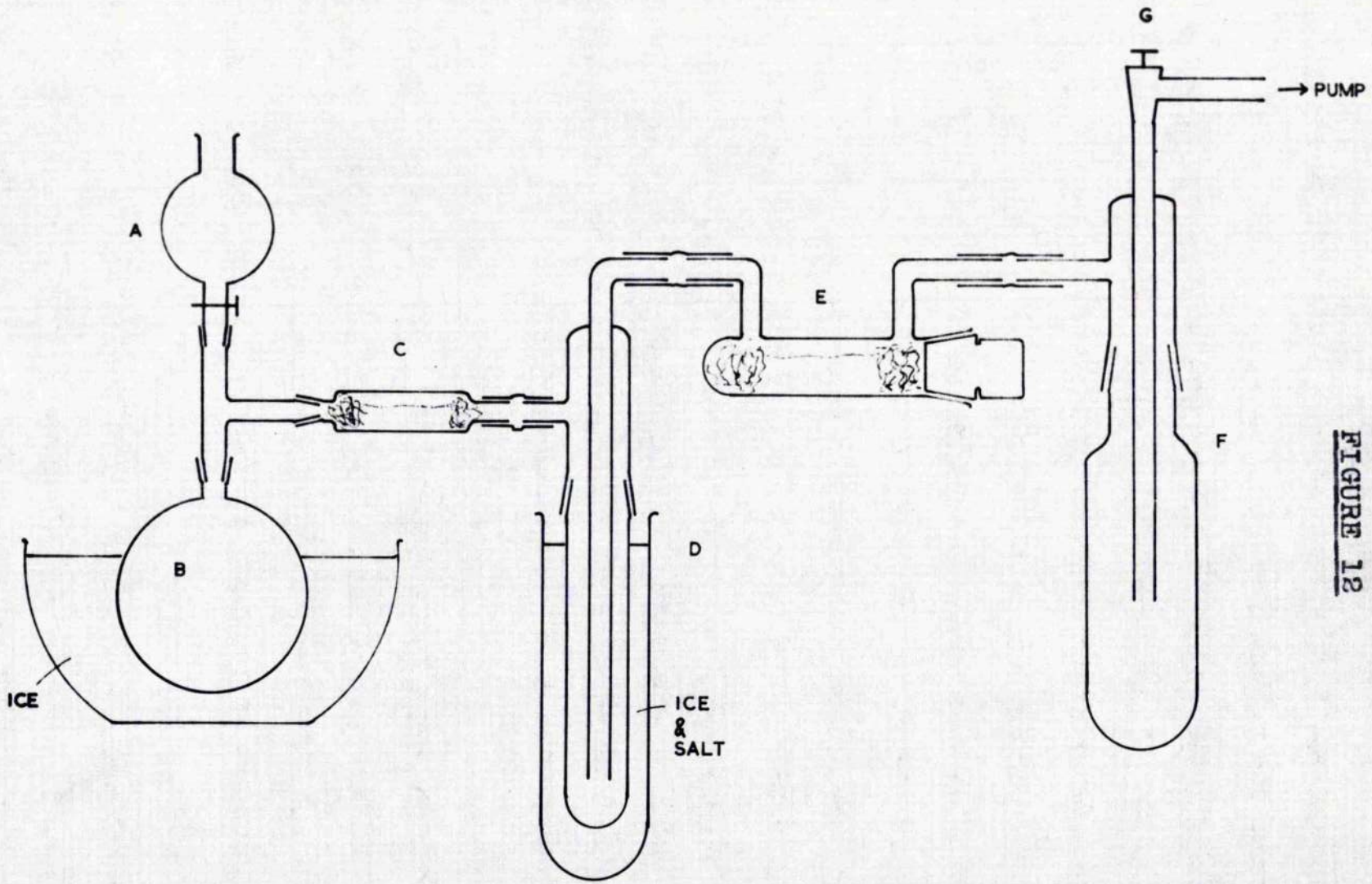


FIGURE 12

sodium and distilled using a long Fenske column. The fraction boiling within 0.1°C of the boiling point at the existing atmospheric pressure was collected.

Hydrogen Iodide. Dry HI was prepared using the apparatus shown in figure 12. A 55% solution of hydriodic acid in the dropping funnel A was added dropwise to solid P_2O_5 in the flask B. The issuing gas passed through a P_2O_5 filled tube C, through trap D cooled in ice and salt in order to remove free iodine, into another P_2O_5 filled tube E, and then through trap F cooled to -185°C where the HI collected as a dirty white solid. Trap F was then sealed and connected to the vacuum system. The impure HI was distilled from -80° to -185° from trap to trap until a white solid free from traces of iodine was obtained. It was stored in black painted bulbs. Because of the reactivity of HI, all taps with which it came in contact were lubricated with silicone grease and picien wax was used to make all joints.

Benzotrifluoride. British Drug Houses "laboratory reagent" benzotrifluoride was distilled in a long glass column, the fraction boiling at 102.2° to 102.5°C being collected. It was then fractionally frozen, about one third being discarded and was dried over $CaCl_2$.

Hexafluoroethane. A gift was received from I.C.I. General Chemicals Division of a cylinder containing a mixture of CF_4 and C_2F_6. The mixture of gases was condensed into a trap at -185°C where the vapour

pressure of CF_4 is about 0.9 mms. The gases volatile at -185°C were pumped off into a large flask until the pressure was 5×10^{-2} mms. Pumping was then continued using the vacuum pumps until the pressure over liquid oxygen fell to 10^{-4} mms. The residual material was found to have a vapour density of 69.2 (for C_2F_6, V.D. = 69.0) and a mass spectrum of the material detected no impurity. However, when, in 1958, an infra red spectrometer became available, it was found that traces of perfluoropropane and perfluoropropylene were also present. These traces should not affect the use of the C_2F_6 as a standard for mass spectrometry.

Fluoroform. Fluoróform was prepared by the action of alcoholic KOH on CF_3I[95]. 15 gms. of KOH pellets and 10 mls of ethyl alcohol were placed in a 500 ml. flask fitted with a seal off and a breakseal. The flask was cooled to -185°C and was evacuated through the seal off. Approximately 0.02 moles of CF_3I were distilled in and the flask sealed. It was shaken for three hours and the breakseal then attached to the vacuum system. The flask was cooled to -80°C and the breakseal broken, allowing the CF_3H to distil into a trap cooled in liquid oxygen and containing sodium. The CF_3H was allowed to warm up, was frozen down again and was pumped several times in order to remove any hydrogen which might be formed if alcohol had distilled away from the -80°C bath; it was then distilled into a 500 ml. flask fitted with a tap. Mass spectrometer analysis detected no impurity, the vapour density was found to be 35.0 (CF_3H, V.D. = 35.0) and the infra red spectrum agreed

with that of Flyler and Benedict [96].

Iodine. The resublimed iodine used was manufactured by May and Baker and was of not less than 99.5% purity. Apart from prolonged pumping at -80°C to remove traces of chlorine and bromine, no further purification was thought necessary.

Analysis of the Products.

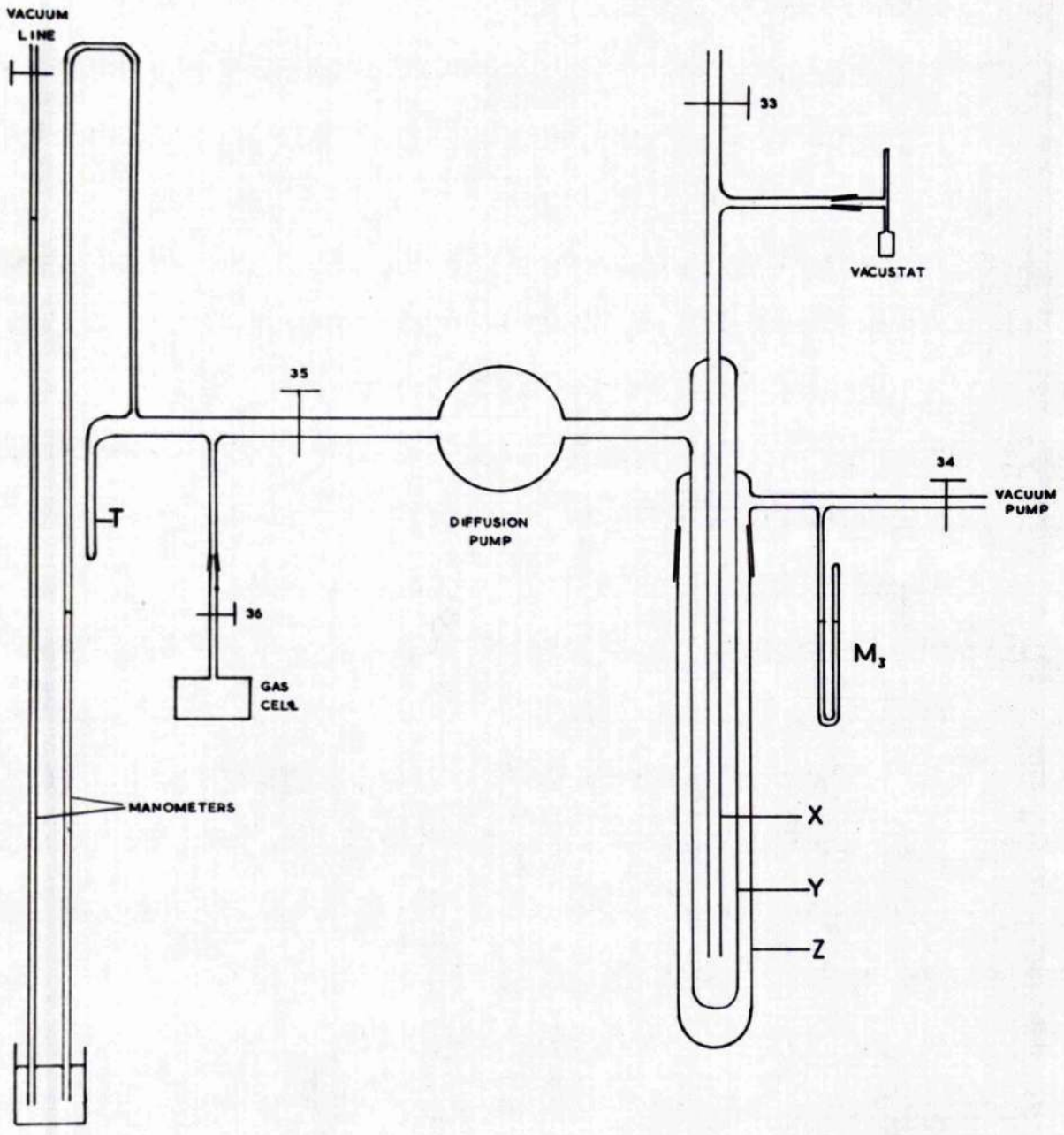
Iodine and Benzyl Iodide. Trap T_1 was cooled to -80°C and in this trap condensed iodine, benzyl iodide and most of the toluene. It was washed out using methanol which had been purified by refluxing over charcoal and subsequent distillation. Aliquots were titrated for iodine using N/100, N/500 or N/1000 sodium thiosulphate solution. When the quantity being estimated was less than about 5.10^{-5} equivalents, the amperometric method of Faulk and Bowden[97] was used; in other cases starch indicator was used to detect the end point.

Benzyl iodide was estimated by oxidation of aliquots of the iodine -benzyl iodide mixture using bromine in a sodium acetate-acetic acid buffer.[98] This oxidises iodine and many iodides to iodate. (Trifluoromethyl iodide and phenyl iodide are unaffected). Excess bromine was removed by using formic acid and addition of potassium iodide and sulphuric acid liberated iodine which was titrated against standard thiosulphate. Subtraction of the known amount of iodine gave the quantity of benzyl iodide.

Hydrogen Iodide. In trap T_2 cooled to -185° condensed HI, C_2F_6, CF_3H, CF_3I and the remainder of the toluene. When HI was present, it

FIGURE 13

LOW TEMPERATURE DISTILLATION APPARATUS



was usually distilled into degassed methanol in trap T_5 cooled to -185°C. Tap 32 was then shut and the methanol allowed to melt; the HI passed into solution. It was then refrozen, T_5 removed and water added. When mass spectrometer analyses were to be made for C_2F_6 and CF_3H, aqueous caustic soda was used instead of methanol, and the volume of T_5 was such that the pressure remained less than atmospheric. The HI was then estimated in a manner similar to that used for benzyl iodide.

Toluene and Benzotrifluoride were frozen out in liquid air in trap T_2 in calibration runs, trap T_1 being at room temperature. They were then distilled into T_5 and estimated by weighing.

Hexafluoroethane and Fluoroform. Two distinct analysis methods were used here, depending on the materials present.

(i) Hexafluoroethane in Trifluoromethyl Iodide. Analysis of C_2F_6 in a mixture containing only C_2F_6 and CF_3I was made by low temperature distillation using a still similar to that described by Le Roy[99]. This method was also used by Dacey[49]. Figure 15 illustrates the still and ancillary apparatus. The still consists of a trap (tubes X and Y) ring-sealed into tube Z which is fitted with a B 34 standard joint. Four chromel-alumel thermocouples were held on to tube Y with "Sellotape" and round this was wound lead foil. The foil was covered with asbestos paper and wound with nichrome tape at 1 cm. spacing. The space between Y and Z could be evacuated by an oil pump connected via tap 34 and the pressure read on manometer M_5. The still was

FIGURE 14a

ABSORPTION OF CF_3I

14·7 mms CF_3I IN GAS CELL

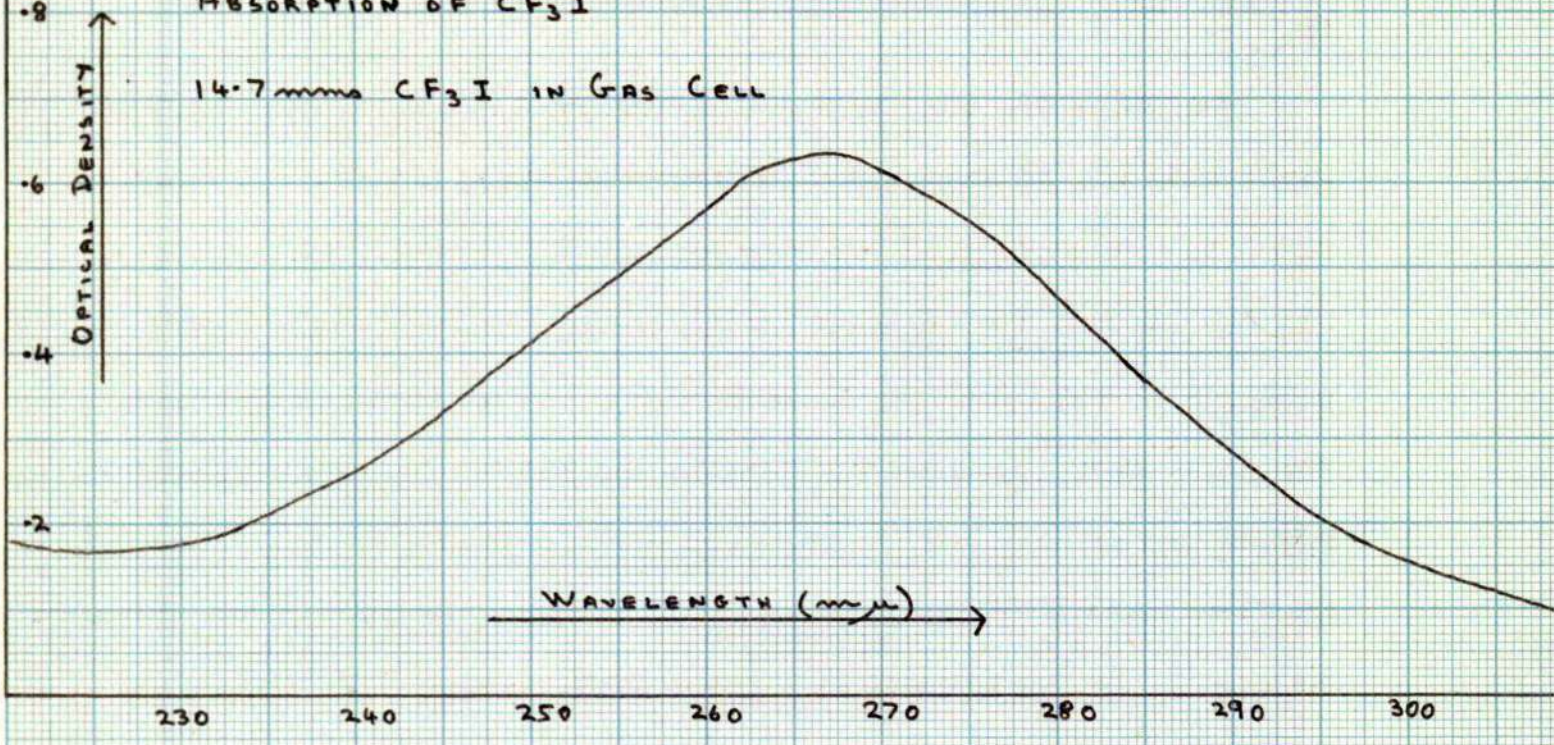
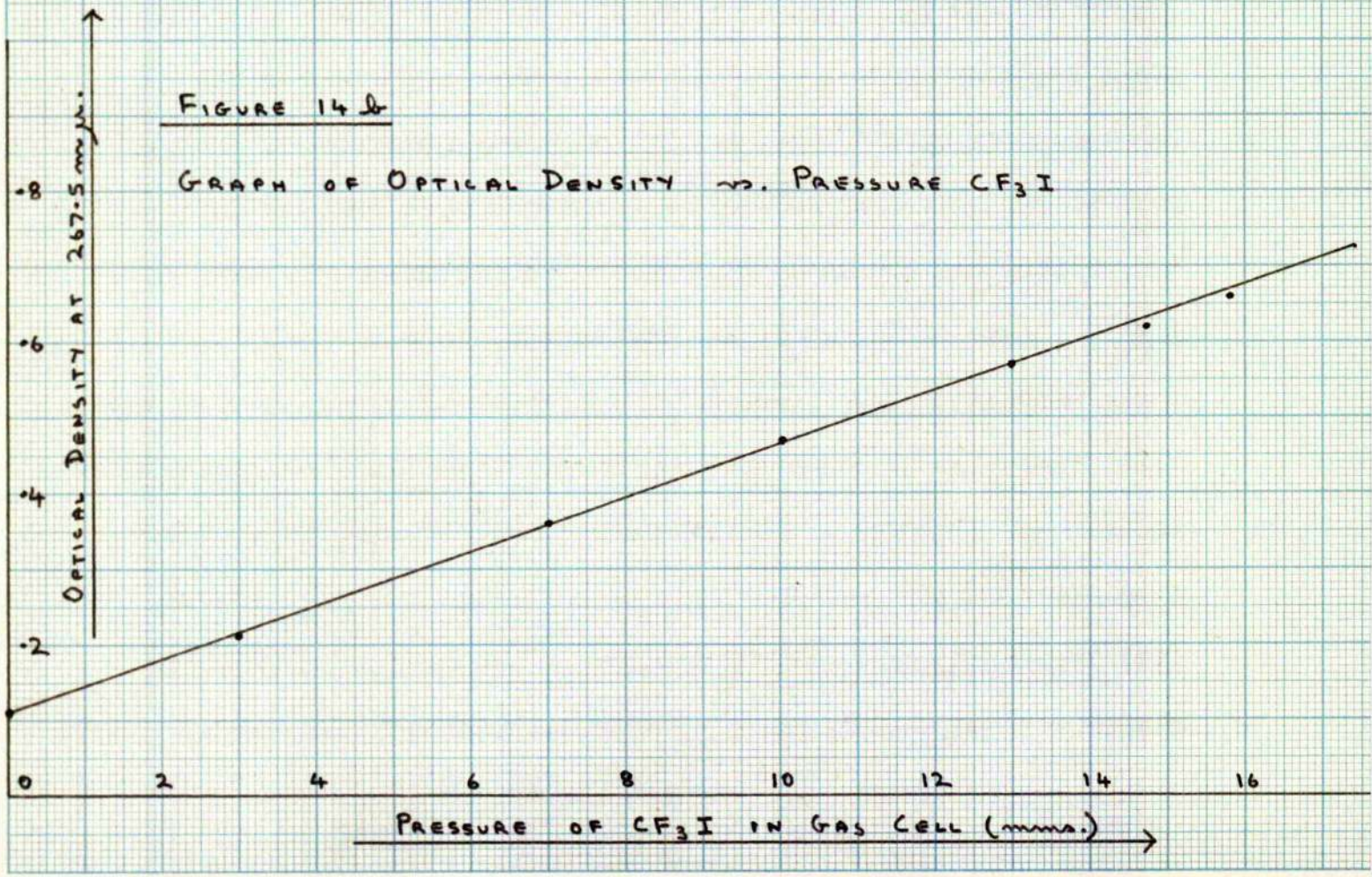


FIGURE 14b

GRAPH OF OPTICAL DENSITY vs. PRESSURE CF_3I



sealed on to one of the four product collection trap systems via tap 35.

The still was used by freezing the CF_3I - C_2F_6 mixture into the still with the YZ space at atmospheric pressure and liquid oxygen round Z. The YZ space was then evacuated to about 2 mms. pressure via tap 34, and the nichrome heater turned on. When the steady pressure in the still was about 0.15 mms. as measured on the vacustat, the small diffusion pump was started and the volatile gas pumped beyond tap 35 to the small tube T cooled in liquid oxygen. When the pressure had fallen to 0.002 mms, tap 35 was shut and the gas allowed to warm up in the calibrated volume. The volume, temperature and pressure noted. Tap 36 was then shut, the gas cell removed from the apparatus, and the absorption at 267.5 mμ was measured on a Unicam SP500 Spectrophotometer. This is the wavelength of maximum absorption of CF_3I[100] (figure 14a) and from the graph of pressure of CF_3I in the cell against optical density (figure 14b) it was possible to estimate the amount of CF_3I which had distilled over with the C_2F_6. There is no absorption due to C_2F_6 at this wavelength. From these readings it was possible to calculate the amount of C_2F_6 made. Tests were done in which the temperature of distillation was altered so that the quantity of CF_3I distilled with the C_2F_6 varied, and consistent values were obtained for the amount of C_2F_6 present.

(ii) Hexafluoroethane and Fluoroform in Trifluoromethyl Iodide.

Mixtures of CF_3H, C_2F_6 and CF_3I were analyzed for CF_3H and C_2F_6 using

GAS BURETTE

FIGURE 15c

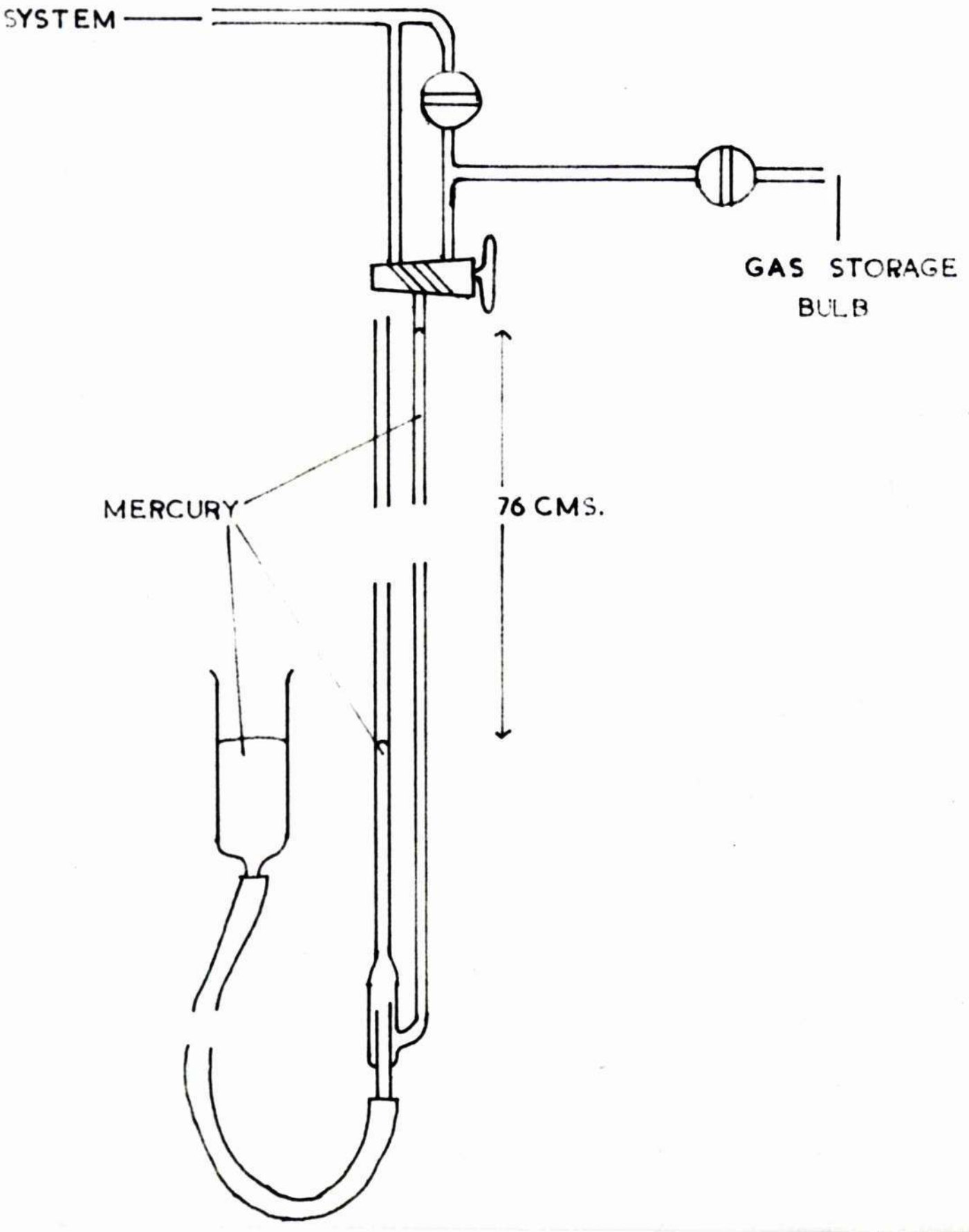


FIGURE 15b

SOLENOID CUT-OFF

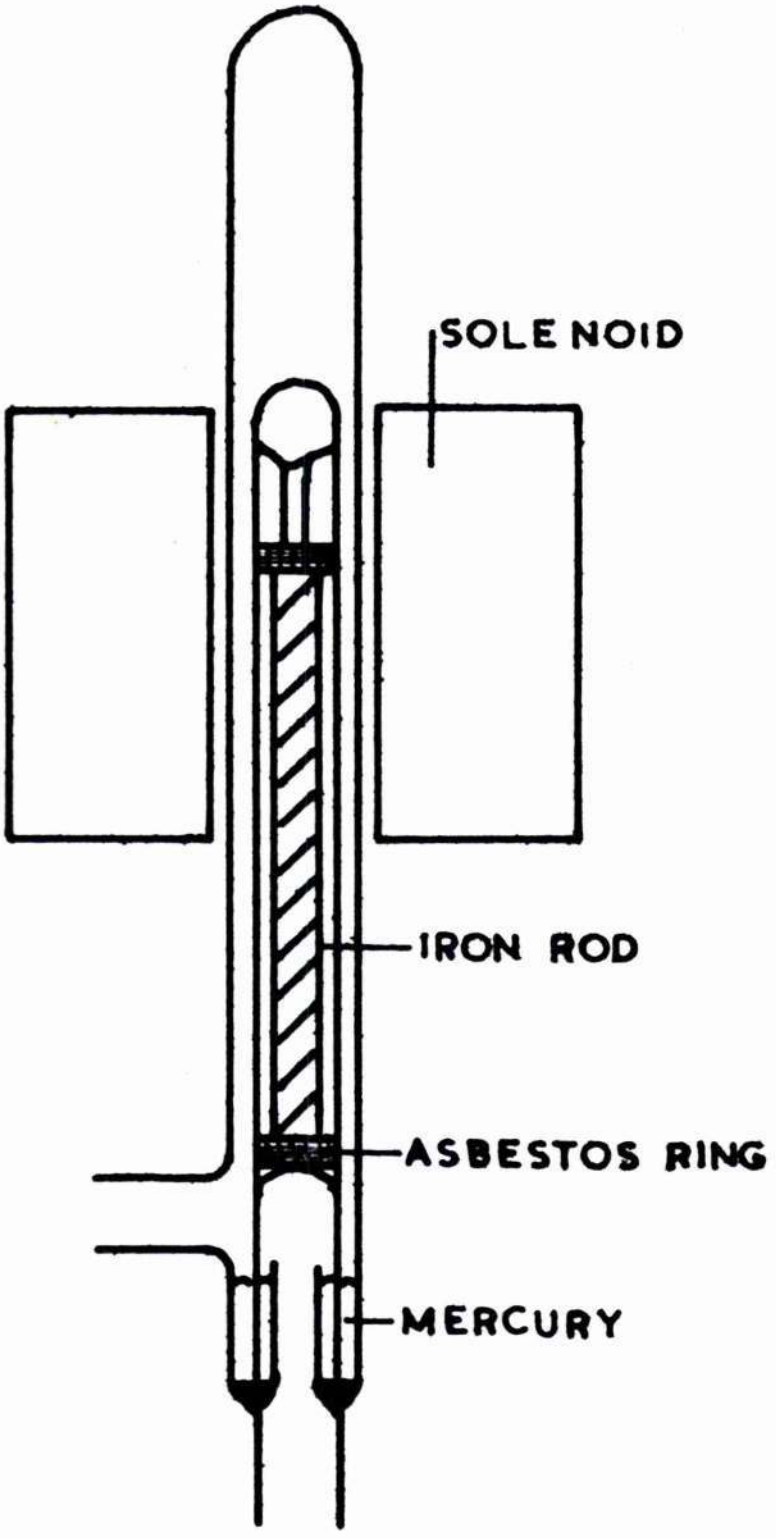
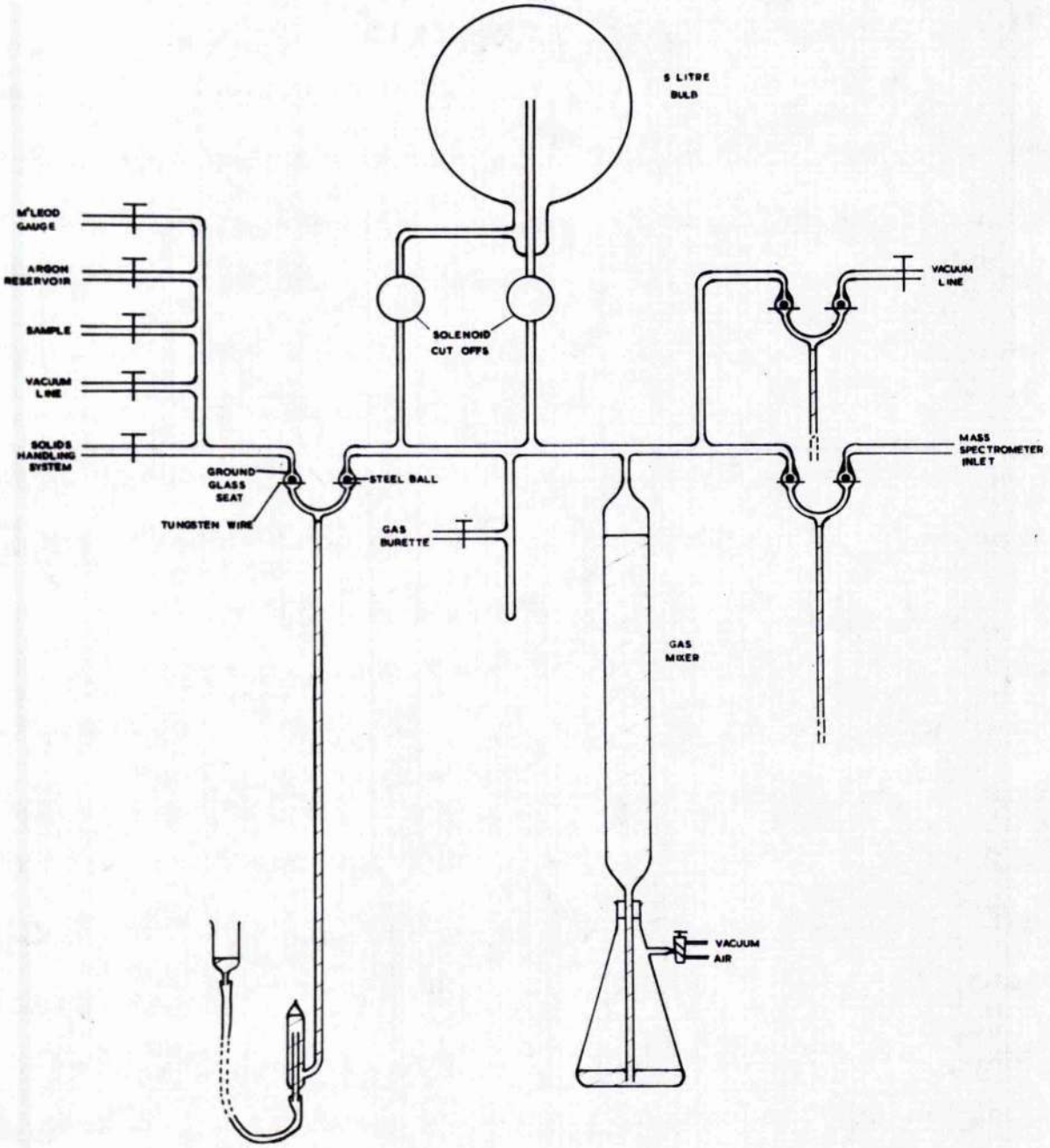


FIGURE 15a

MASS SPECTROMETER GAS HANDLING SYSTEM



a 60° Nier type mass spectrometer constructed in the department. The mass spectrometer was calibrated for CF_3H and C_2F_6 sensitivity against argon as standard. The gas handling system is shown in figure 15a, and figures 15b and 15c show the solenoid valves used in the gas handling system, and the gas burette respectively.

In order to reduce the amount of tap grease in the gas handling system, mercury cut-offs capable of withstanding one atmosphere pressure were used. These consisted of ground glass seats into which stainless steel balls fitted. The cut-off was closed by raising the mercury level and floating the steel balls into the ground seats; when the mercury was lowered to open the cut off, the balls were prevented from falling down the tubes by tungsten wires sealed into the glass. The solids handling system contained a McLeod gauge and a metrosil leak into the mass spectrometer; in this case it was used merely as a convenient means of introducing argon into the mass spectrometer. Known amounts of CF_3H were injected from the gas burette into the gas handling system and the CF_2H^+ peak at $\frac{m}{e} = 51^+$, the A^+ peak with $\frac{m}{e} = 40^+$ and the argon pressure were measured. Similar calibrations were made with CF_3I in the system, correction being made for the $C^{13}F_2^+$ isotope peak from the CF_3I. The rather scattered straight line (figure 16a) was obtained on correcting the results to constant argon sensitivity. Calibrations were also performed for C_2F_6, the measurements being made on the $C_2F_5^+$ peak at $\frac{m}{e} = 119^+$. (figure 16b).

FIGURE 16b

SENSITIVITY OF MASS SPECTROMER TO C_2F_6 AT CONSTANT ARGON SENSITIVITY.

• = C_2F_6 ALONE

× = C_2F_6 IN PRESENCE OF CF_3I

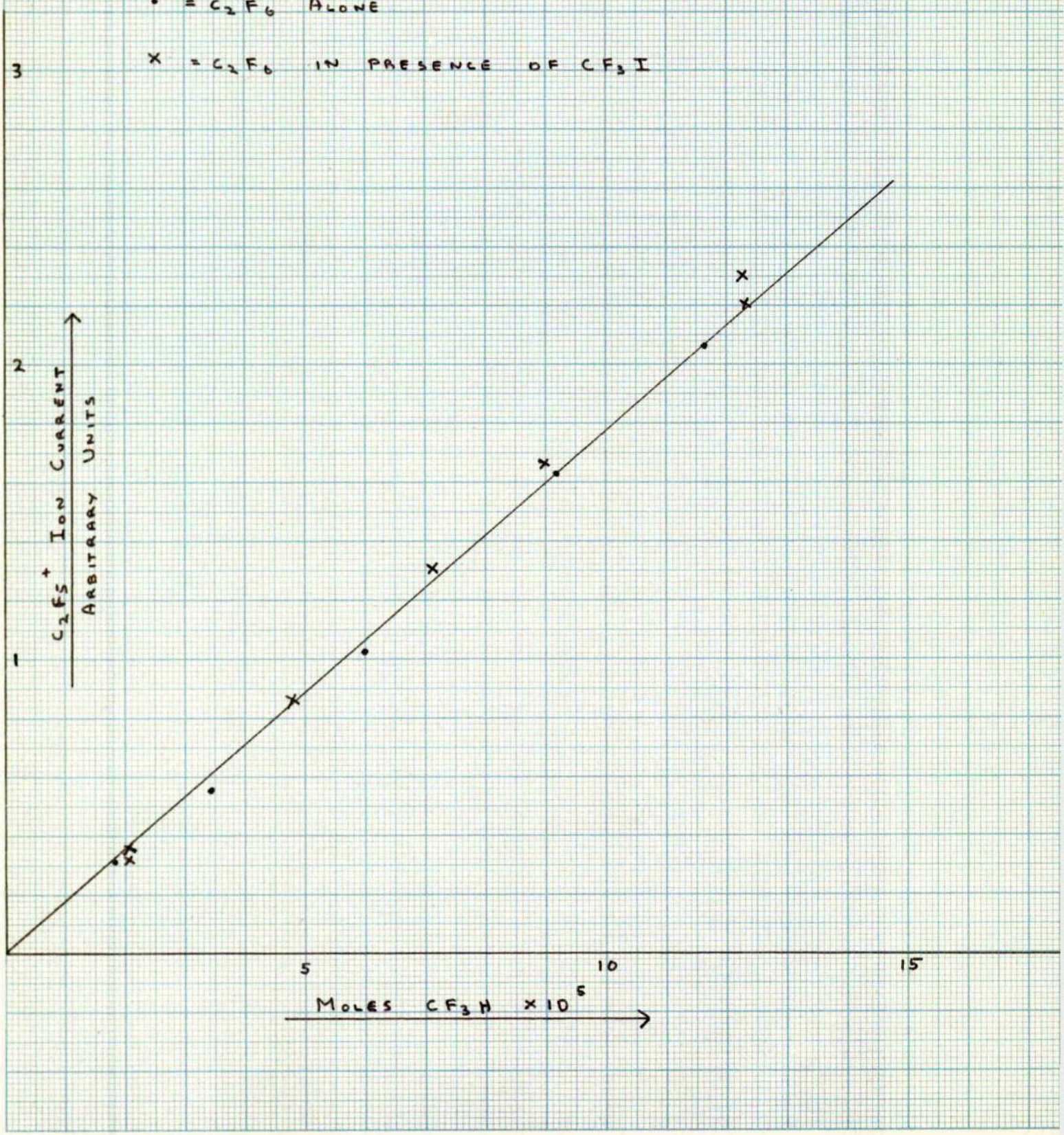
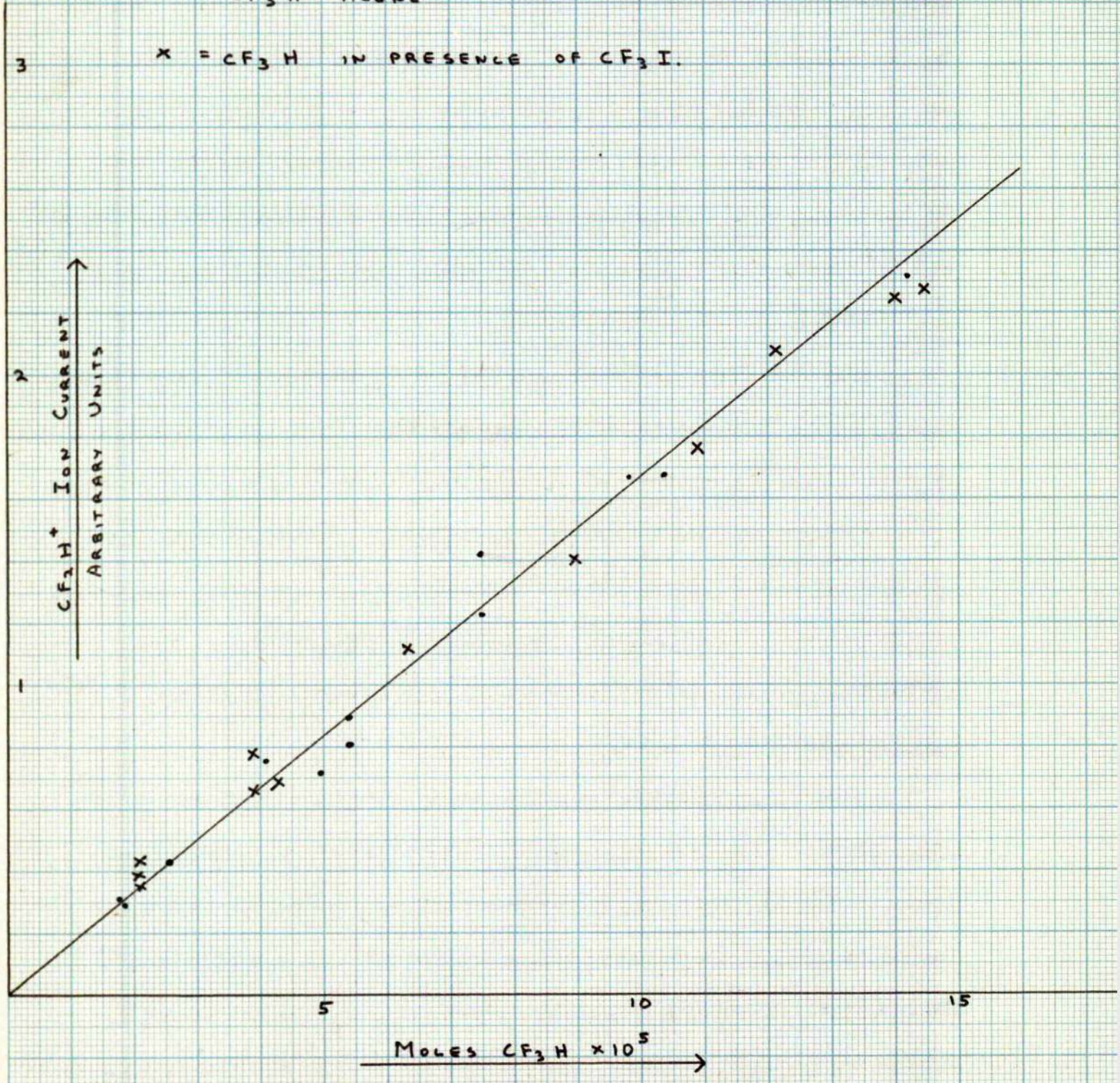


FIGURE 16a

SENSITIVITY OF MASS SPECTROMETER TO CF_3H AT CONSTANT ARGON SENSITIVITY.

• = CF_3H ALONE

× = CF_3H IN PRESENCE OF CF_3I.



An analysis was performed by distilling the mixture of CF_3I, C_2F_6, CF_3H, HI and in some cases a little toluene condensed in trap 2 into trap 3 which contained aqueous degassed NaOH solution. This removed almost all the HI. The mixture or an aliquot was admitted to the handling system, mixed, and the 40^+, 51^+ and 119^+ peaks were measured; the pressure of argon in the solids handling system was also read. The 51^+ peak from CF_3I was subtracted from the total 51^+ peak and when toluene was present, allowance was made for the 40^+ and 51^+ peaks from toluene. From these readings, the amounts of CF_3H and C_2F_6 could be calculated.

After the first few analyses had been performed in this manner, it was found that the relative sensitivities of the mass spectrometer, CF_3H to A and C_2F_6 to A, had altered about 12%. Accordingly, the mass spectrometer was calibrated by injecting known amounts of CF_3H and C_2F_6 into the sample being analyzed, mixing the gases, and using the increase in peak height to measure the sensitivity of the instrument. This method should give more accurate readings.

Description of an Experiment.

Before an experiment, the apparatus was pumped for one to two hours with the furnace hot and liquid air on the circulating pump traps. The CF_3I was frozen from the storage bulb into reservoir A cooled in liquid oxygen and, after outgassing was brought to $-78^\circ C$. The methanol or sodium hydroxide solution in T_3 was outgassed by successive coolings, pumpings and meltings. In the experiments using

toluene, the toluene was degassed, the injection valve heated, and the thermostat bath brought to the desired temperature. Benzotrifluoride was similarly treated. When HI was being used, some was frozen from the storage bulb into the injection reservoir cooled to -185°C. Any non condensable gas was pumped out, taps 27 and 29 closed and the reservoir warmed to -78°C; at this temperature the HI vapour pressure was 60 mms. Iodine was introduced using the saturator system and the saturators were kept at -185° until it was desired to start injection.

After isolation of the flow line, the desired amount of carrier gas was introduced by use of the manostat and the circulating pump was started; the gas flow was directed through the spare trap and the hot sodium trap. Suitable refrigerants were placed round all the traps in the system and after the gas had circulated over hot sodium for about one hour to remove traces of oxygen, the sodium trap was isolated and the gas passed through tap 6.

Once the desired steady flow conditions had been obtained, the reactants were injected and the flow changed from trap to trap in the manner most suitable to allow for calibration measurements and actual decomposition runs to be performed. The U tube U_1 at the entrance to the furnace was cooled in liquid oxygen when it was desired to stop CF_3I alone entering a glass reaction vessel. The spare trap was used to allow conditions to settle after injecting another material, and in the runs using $PhCH_3$, HI, $PhCF_3$ and I_2 one of the product collection

traps was often used to measure the amount of material injected.

At the end of an experiment, all the injections were stopped, the furnace was switched off and the gas was circulated for a few minutes through the spare trap to sweep any condensables out of the system. The system was then pumped out to 10^{-4} mms. or better, and the CF_3I distilled, by closing the appropriate taps, from trap T_7 to the calibrated volume and manometer beyond tap 51. It was then allowed to warm up to room temperature and the pressure, volume, and temperature measured. The toluene in the calibration trap was distilled into T_5 and weighed (as was $PhCF_3$); the HI was distilled into degassed methanol. The system was then let down to atmospheric and the other products washed out.

Calculation of the Results.

The following relationships were used to calculate partial pressures and contact times.

Total moles/sec = moles/sec A + moles/sec B + -----

$$\text{Partial pressure of A in mms} = \frac{\text{moles/sec of A}}{\text{Total moles/sec}} \times P_F$$

where P_F = pressure in reaction vessel in mms.

Total pressure = partial pressure A + partial pressure B + -----

The rate of flow in mls./sec. was calculated from

$$\text{mls./sec.} = \text{moles/sec} \times 22400 \times \frac{760}{P_F} \times \frac{T}{273}$$

where T = temperature of reaction vessel in ^{o}K.

$$\text{Contact Time} = \frac{\text{Volume of Reaction Vessel in mls.}}{\text{Rate of flow in mls./sec.}}$$

The Static Reaction System.

The high pressure runs were carried out in sealed bulbs. The reactants and methods of analysis were the same as had been used in the flow system and the same vacuum line was employed. The differences in apparatus and technique are described below.

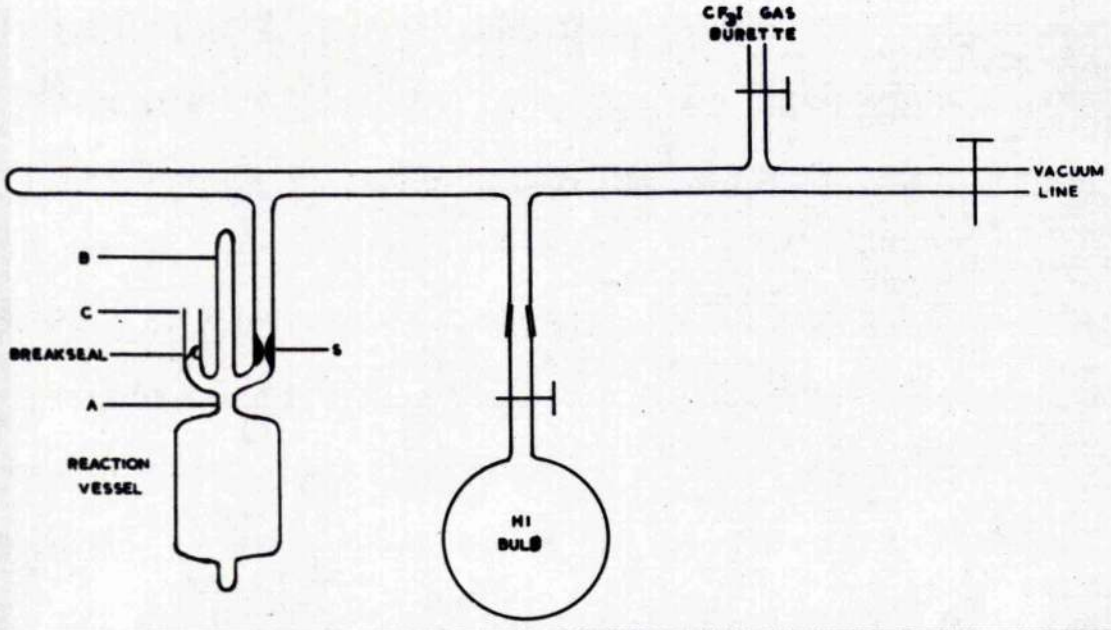
The Reaction Vessels. Three reaction vessels were constructed with dimensions as similar as possible. They were made of 30 mm. diameter pyrex tubing narrowed down to 12 mm. diameter at each end. (figure 17). The 12 mm. piece of tubing at one end was sealed off so that reactants could be frozen into it; the other was used to attach a breakseal and seal off at A. The volumes of the vessels were 690 mls., 702 mls. and 706 mls.; each was taken as having volume = 700 mls. for the purposes of calculations.

The Furnace. The furnace consisted of a two feet long, four inches diameter iron tube wound with Brightray C similar to the flow system furnace. The temperature was uniform to $\pm$ 1 C° over the central 10 inches length; no temperature variation was found in a vertical plane. The reaction vessels were placed symmetrically about the centre of the furnace. A Sunvic RT2 furnace controller using a circuit similar to that in figure 5 controlled the temperature which was measured by a chromel alumel thermocouple. Both the resistance thermometer for the controller and the thermocouple junction were clamped mid-way along the furnace near the top.

FIGURES 17a and 17b

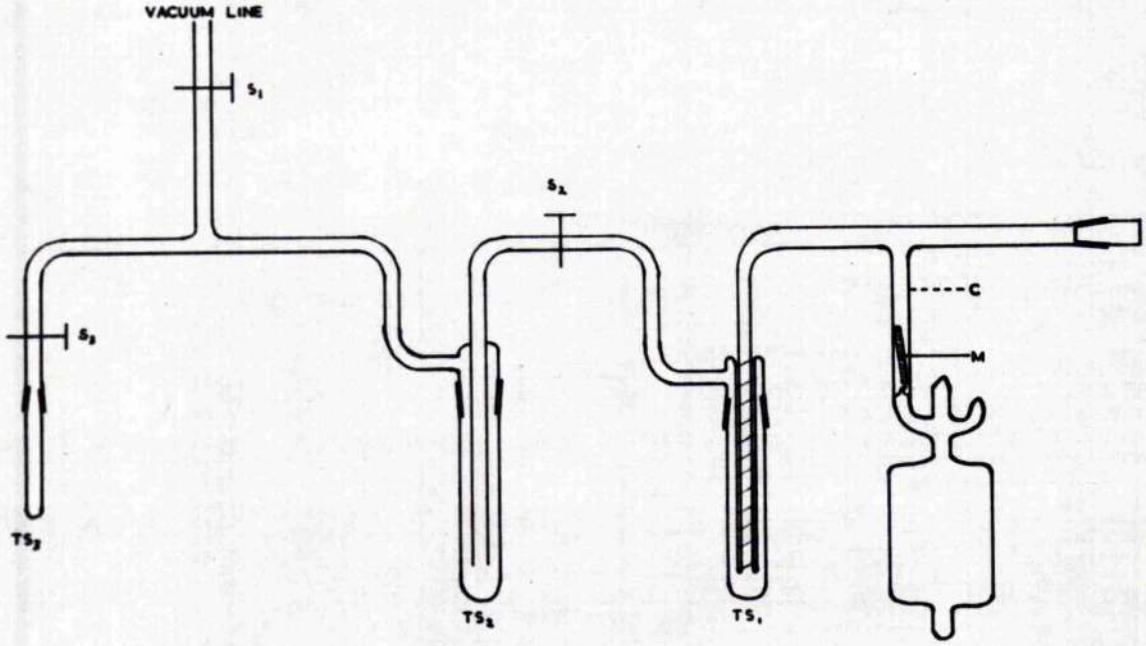
FILLING STATIC REACTION VESSELS

FIGURE 17a



EMPTYING STATIC REACTION VESSELS

FIGURE 17b



Measurement of Reactants.

Trifluoromethyl Iodide was measured out using the gas burette previously employed for calibration of the mass spectrometer to CF_3H and C_2F_6. It was not estimated among the reaction products.

Hydrogen Iodide. Some HI was frozen down from the storage bulbs into a small tube. It was allowed to evaporate from the tube into a detachable bulb of known volume fitted with a tap. When the pressure as read on a U tube manometer was such that the desired amount of HI was in the bulb, the tap on the bulb was shut. Unused HI was then distilled back into the storage volume and the detachable bulb removed. The HI was also estimated at the end of an experiment.

Iodine. In some experiments, a weighed amount of iodine was added to the reaction vessel. In trial experiments, the amount of iodine recovered from a reaction vessel after going through the experimental procedure varied from 1% above to 8% below the weighed amount. The weighed amount was used in calculations.

Description of an Experiment.

Reactants were introduced to the reaction vessel using the apparatus shown in figure 17a. The system was evacuated and the vacuum tap shut. CF_3I was measured from the gas burette and distilled into the reaction vessel, the bottom of which was cooled in liquid oxygen. The HI which had been previously measured into the bulb was then allowed to distil into the reaction vessel, the pumping tap opened to remove any non condensable gases, and the flask sealed at S.

When iodine was added, a slightly different method was used. The apparatus was evacuated as before to remove any condensable impurities. It was then let down to atmospheric through a liquid air trap, tube B cut near the top, and the small tube containing the weighed amount of iodine lowered into the reaction vessel. Tube B was resealed, care being taken not to allow the flame near the top of the tube, the reaction vessel was cooled to -185°C and the system evacuated. The CF_3I and HI were then introduced as before and the vessel sealed.

Once the reactants had evaporated inside the vessel, it was placed in the furnace which was at the desired reaction temperature. The furnace temperature fell on the introduction of the reaction vessel and did not regain temperature for about twenty minutes. The time of reaching 5 C° below the desired temperature was taken as the start of the reaction. Since the minimum reaction time used was three hours, this should cause no serious error. After the experiment had proceeded for the intended time, the reaction tube was removed and allowed to cool.

The reaction vessels were emptied and the products collected by means of the apparatus shown in figure 17b. Trap TS_1 had a nichrome tape heater wound in the interspace of the double walled centre tube; this made iodine condense out at a suitable place in the trap. Trap TS_3 contained methanol. In use, the reaction vessel was attached at C with the glass enclosed magnetically operated hammer M introduced

as shown. The system was evacuated and the methanol in trap TS_5 outgassed. Tap S_1 was then shut and traps TS_1 and TS_2 cooled to -80° and $-185^{\circ}C$ respectively. The break-seal was then smashed and the products distilled out. Tap S_2 was then shut, the liquid oxygen removed from around trap TS_2 and the contents of the trap distilled into the degassed methanol in TS_5 where they dissolved on warming up. The methanol was then refrozen, tap S_5 shut, trap TS_5 removed and water added. The contents were analysed for HI. The iodine in trap TS_1 was washed out with purified methanol and estimated.

EXPERIMENTAL RESULTS.

Flow System Experiments.

The Decomposition of Trifluoromethyl Iodide Alone in a Nickel Vessel.

For the first experiments, a nickel reaction vessel was used in the hope that there might be no reaction between CF_3 radicals and the walls of the reaction vessel. Preliminary decompositions were performed using CF_3I which had about 2% of C_2F_5I as impurity. Using this material, experience was gained in the operation of the apparatus and a suitable temperature for decomposition was found. None of these experiments are quoted.

CF_3I free from C_2F_5I was prepared by distillation of the CF_3COOH used in the synthesis, and with this material, some quantitative experiments were performed.

The Products of the Reaction.

The only product found in the trap cooled to -80° was iodine. The material condensing in trap 2 at $-183^{\circ}C$ was analysed qualitatively on the mass spectrometer. It appeared to consist of CF_3I and C_2F_6 only, the C_2F_6 being identified from the peak with $\frac{m}{e} = 119^{+}$. No peak was found at $\frac{m}{e} = 81^{+}$; this peak, due to the ion $C_2F_3^{+}$, is 70% of the main peak of C_2F_4 but is only 0.1% of the main peak from C_2F_6. This indicates that no C_2F_4 was produced. There was no peak due to the ion $CF_2I_2^{+}$ so this material was not formed either. No evidence was found for higher fluorocarbons, but the mass spectrometer is not very suitable for their analysis as few peaks of high m/e ratio are formed from them.

However, some black material was found on a piece of nickel foil placed inside the reaction vessel and oxidation of this substance produced CO_2; it appeared to be mainly carbon. The nitrogen carrier gas was examined for CF_4 and F_2 but none was found. Quantitative analysis of the material condensed at -183°C was performed using the low temperature still. Only one sharp increase in vapour pressure was found as the temperature was raised, and analyses were performed assuming that all the volatile material was C_2F_6. The method is not specific for C_2F_6, but at the time, no pure C_2F_6 was available and the department did not then possess an infra red spectrometer. In general, it was found that the C_2F_6 recovered was about 90% of the iodine found, and most of the reaction would appear to proceed according to the stoichiometric equation

$$2\,C\,F_3\,I \longrightarrow C_2F_6 + I_2$$

Some decomposition of either CF_3 radicals or CF_3I must also take place to give carbon.

During this work on the reaction products, the reaction time was varied. The results are given in table 3 and plotted in figure 18. The percentage decompositions were worked out from the iodine found.

TABLE 5 Variation of Contact Time

Temperature = 524°C = 797°K

Nitrogen Carrier Gas Pressure 4.99 to 5.60 mms.

Expt. No.	Contact Time (secs)	Pressure CF_3I (mms.Hg)	Equivs $I_2 \times 10^4$ formed	Percent. Decomp.	Moles $C_2F_6 \times 10^5$ found	Moles C_2F_6 / Moles I_2
1a	1.16	.288	1.77	6.78	8.14	.92
b	1.16	.288	1.88	7.20	7.94	.87
c	1.16	.288	1.87	7.16	8.15	.87
2a	1.07	.270	1.42	5.46	6.85	.97
b	1.07	.270	1.59	6.11	7.02	.88
c	1.07	.270	1.62	6.25	7.02	.86
5a	1.55	.379	1.80	6.84	7.7	.86
b	1.55	.379	1.77	6.75	8.3	.94
c	1.55	.379	1.81	6.88		
4a	.794	.190	1.22	5.05	5.36	.88
b	.794	.190	1.24	5.11	5.80	.94
c	.794	.190	1.25	5.15		
5a	1.44	.249	1.20	6.56	5.2	.87
b	1.44	.249	1.25	6.50	4.6	.75
c	1.44	.249	1.24	6.56		
6a	1.89	.289	.98	6.32		
b	1.89	.289	1.07	6.90		
c	1.89	.289	1.14	7.35		

Table 3 con.

Expt. No.	Contact Time (secs)	Pressure CF_3I (mms.Hg)	Equivs $I_2 \times 10^4$ formed	Percent. Decomp.	Moles $C_2F_6 \times 10^5$ found	Moles C_2F_6 / Moles I_2
7a	.627	.215	1.25	3.55		
b	.627	.215	1.45	4.24		
c	.627	.215	1.41	4.15		
8a	.610	.254	1.68	4.55	8.58	1.00
b	.610	.254	1.62	4.39	7.99	.99
c	.610	.254	1.68	4.55		
9a	.445	.257	1.76	2.94	8.20	.93
b	.445	.257	1.82	3.04		
c	.445	.257	1.85	3.05		
10a	2.20	.242	.78	6.75		
b	2.20	.242	.88	7.61		
c	2.20	.242	.85	7.35		
*11a	.740	.262	1.85	4.95		
b	.740	.262	1.95	5.34		
c	.740	.262	1.94	5.31		
*12a	.724	.242	1.93	5.50	8.14	.85
b	.724	.242	1.87	5.44		
c	.724	.242	1.90	5.41		

* indicates an experiment carried out after oxidation of the nickel reaction vessel.

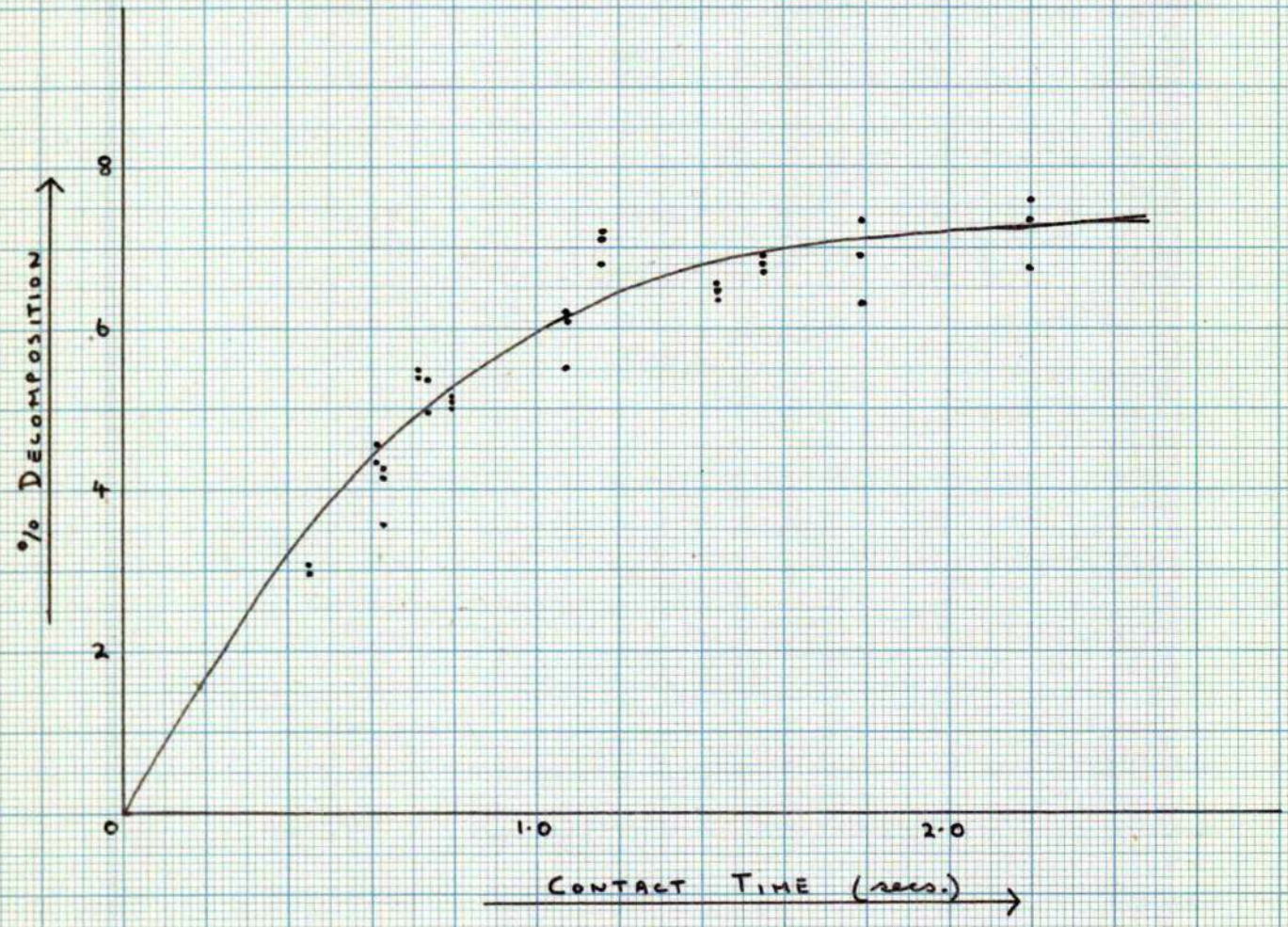
FIGURE 18

PERCENTAGE DECOMPOSITION vs. CONTACT TIME

797°K NICKEL REACTOR

CF_3I PRESSURE .190 to .379 mms.

N_2 CARRIER GAS PRESSURE 4.99 to 5.6 mms.



After experiment 10, an attempt was made to estimate the amount of carbon formed by circulating oxygen through the hot reaction vessel and measuring the CO_2 formed. However, CO_2 continued to be produced at an appreciable rate for more than twelve hours. The U tube, U_1, at the furnace inlet was cooled in liquid oxygen in order to condense out any gas from the tap grease which might be oxidised and cause this effect. The rate of formation of CO_2 was only slightly diminished. It was then realized that the small percentage of carbon in the nickel was being oxidised so that estimation of the carbon formed in the reaction would not be feasible by this method. Experiments 11 and 12 were performed to see if oxidation of the nickel had affected the rate. No marked effect was found.

From figure 18 it is seen that the rate falls off considerably as the reaction proceeds. If we use the tangent to the curve as a measure of the rate, there is a fall to about $1/16^{th}$ of the initial rate after a two second reaction time during which the initial concentration of reactant has fallen by only 7 to 8%. This is much too rapid a decrease in rate to be accounted for by any simple rate law involving a small numerical power of the iodide concentration, and it suggests inhibition by products. The most obvious method of accounting for these facts is the following free radical mechanism.

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

$$I + C F_3 \longrightarrow C F_3 I \qquad (2)$$

$$I + I \longleftrightarrow I_2 \qquad (3)$$

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (4)$$

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (5)$$

The amount of iodine builds up as reaction proceeds and the CF_3 radicals formed in the initial split (1) react by reactions (2) and (4) to reform CF_3I. The formation of C_2F_6 in reaction (5) is probably the rate determining step.

The Addition of Toluene.

In order to test the above mechanism, it was decided to inject toluene. Toluene has a weak C - H bond in the side chain and should react with a CF_3 radical:-

$$CF_3 + C_6H_5CH_3 \longrightarrow CF_3H + C_6H_5CH_2 \qquad (6)$$

$$2\,C_6H_5CH_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (7)$$

Thus many, and possibly all of the CF_3 radicals should form CF_3H and since they could not then take part in reactions reforming CF_3I, the percentage decomposition should increase. In these circumstances the rate limiting step should become reaction (1)

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

The benzyl radicals formed are unreactive and should dimerise to form dibenzyl; this is the principle of Szwarc's toluene carrier gas technique.[75]

The toluene injection unit was constructed and inserted into the flow line between the two way solenoid valve and the furnace entry. On injecting the toluene into the hot nickel reaction vessel there was found to be a considerable increase in pressure. The gas formed was

analysed on the mass spectrometer and found to consist of H_2 and CH_4 formed in the catalytic decomposition of toluene on the nickel. Nickel catalysts can be poisoned by sulphur, so a low pressure of hydrogen sulphide was distilled through the hot reaction vessel; this was found to stop the decomposition at the temperature used.

In order to check whether this treatment had affected the rate of decomposition of CF_3I alone, some experiments were performed where no toluene was added; in others, one trap was often used to check the rate of injection of toluene.

The Reaction Products.

In the first few experiments, the only material analysed in trap 1 was iodine. Later it was realized that benzyl iodide was formed under the experimental conditions, since it was detected by its smell and by the quantity of iodine formed on oxidation with bromine.

The liquid oxygen condensable products were analysed qualitatively on the mass spectrometer. It was found that CF_3H was formed but that there was still some C_2F_6 present. Some white solid was found to condense in the exit tube from the furnace. The U tube U_2 was cooled in ice and water to condense this material. It was dissolved in methanol and its ultra violet absorption spectrum examined. The main absorption appeared to be due to stilbene, but there was also some absorption in the region characteristic of dibenzyl. Since the maximum molar extinction coefficient of stilbene is more than one hundred times greater than the maximum molar extinction coefficient

of dibenzyl, the material contained only about 1% of stilbene. In this type of mixture, it is difficult to identify and estimate dibenzyl accurately and no quantitative analyses were performed. The results are given in table 4 and are plotted in figure 19.

TABLE 4 Addition of Toluene

Temperature = 524°C = 797°K N_2 carrier gas 4.21 to 5.55 mms.

Expt. No.	Press CF_3I (mms)	Press. Toluene (mms)	Contact Time (secs)	Moles $CF_3I \times 10^4$ passed	Equivs $I_2 \times 10^5$ formed	Equivs I_2 / Moles CF_3I	Moles C_2F_6 / Moles I_2	Moles $BzI \times 10^5$ formed	I_2+BzI / CF_3I
15	.254	.88	1.51	17.71	32.7	18.5%	-		
14a	.288	-	1.88	16.1	12.9	8.0%	1.04		
b	.288	-	1.88	16.1	12.7	7.9%	.91		
c	.288	-	1.88	16.1	12.5	7.8%			
15	.249	1.05	1.75	15.6	26.6	17.0%	-		
16a	.343	-	2.52	14.3	11.4	8.0%	.96		
b	.343	-	2.52	14.3	12.9	9.0%	.92		
c	.343	-	2.52	14.3	12.6	8.8%	.86		
17a	.290	-	1.65	19.0	16.5	8.7%	.86		
b	.290	-	1.65	19.0	16.5	8.7%	.87		
c	.243	.83	1.43	19.0	31.4	16.5%	-		
18a	.250	-	1.60	10.95	9.9	9.0%	.71		
b	.250	-	1.60	10.95	9.2	8.4%	.75		
c	.212	1.25	1.36	10.95	16.8	15.3%			

FIGURE 19

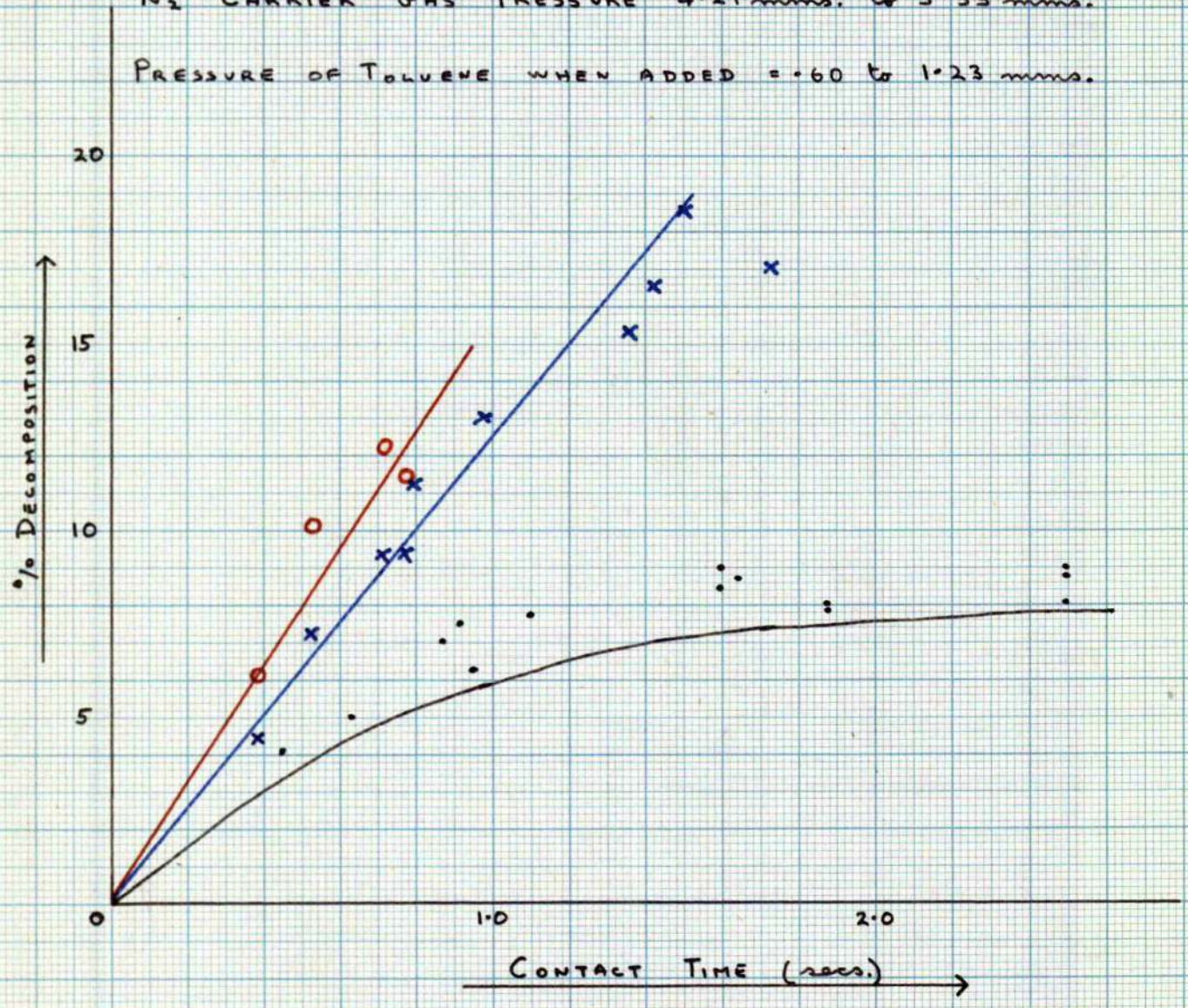
ADDITION OF TOLUENE

797°K NICKEL REACTOR

CF_3I PRESSURE ·212 mms. to ·414 mms.

N_2 CARRIER GAS PRESSURE 4·21 mms. to 5·35 mms.

PRESSURE OF TOLUENE WHEN ADDED = ·60 to 1·23 mms.



—— = LINE FROM EXPERIMENTS 1 to 12

• • = % DECOMPOSITION WITHOUT TOLUENE AFTER SULPHIDING.

× × = % DECOMPOSITION TO I_2 IN PRESENCE OF TOLUENE

○ ○ = % DECOMPOSITION TO $(I_2 + C_6H_5CH_2I)$ IN PRESENCE OF TOLUENE

Table 4 Con.

Expt. No.	Press. CF_3I (mms)	Press. Toluene (mms)	Contact Time (secs)	Moles $CF_3I \times 10^4$ passed	Equivs $I_2 \times 10^5$ formed	Equivs I_2 / Moles CF_3I	Moles C_2F_6 / Moles I_2	Moles BzI $\times 10^5$ formed	$\frac{I_2+BzI}{CF_3I}$
19a	.258	-	1.11	16.51	12.5	7.7%	.82		
b	.229	1.00	.98	16.51	21.2	15.0%			
20a	.254	-	.87	20.6	14.5	7.0%	.88		
b	.225	.93	.80	20.6	23.0	11.2%			
21a	.414	-	.65	45.9	23.0	5.0%	.92	-	
b	.346	.79	.53	34.4	24.9	7.25%		9.7	10.1%
22a	.264	-	.448	30.9	12.7	4.1%	.81	-	
b	.252	.64	.395	30.9	15.6	4.4%		5.5	6.1%
23a	.297	-	.947	25.1	14.6	6.25%	.87	-	
b	.257	.60	.780	23.1	21.6	9.35%		4.45	11.4%
24a	.277	-	.920	21.6	16.2	7.5%	.76	-	
b	.224	1.09	.725	21.6	20.2	9.3%		6.25	12.2%

BzI represents benzyl iodide $C_6H_5CH_2I$

This set of experiments was stopped abruptly when the narrow nickel exit tube of the reaction vessel cracked through. The crack was probably due to embrittlement of the nickel as a result of the treatment with H_2S.

Figure 19 shows that the addition of toluene increases the rate of

decomposition and the reaction

$$C F_3 + C_6 H_5 C H_3 \longrightarrow C F_3 H + C_6 H_5 C H_2 \qquad (6)$$

must proceed since CF_3H is formed and dibenzyl and stilbene are found. The stilbene presumably results from the reaction

$$C_6 H_5 C H_2 C H_2 C_6 H_5 + 2 C F_3 \longrightarrow C_6 H_5 C H = C H C_6 H_5 + 2 C F_3 H$$

The rate of production of iodine and of (benzyl iodide + iodine) seems to be fairly independent of contact time. Nevertheless, the presence of C_2F_6 in the products shows that all the CF_3 radicals have not reacted with toluene and presumably the back reactions (2) and (4) proceed as well.

There appeared to be a little attack of iodine on the nickel, for 8×10^{-5} equivalents of iodine were produced by heating the furnace to 600°C and sweeping nitrogen through the apparatus. This is a negligible amount of iodine when compared to the total iodine produced in all the experiments performed. However, this may account for the average rate of decomposition in the absence of toluene being slightly greater than was found in experiments 1 to 12, and for some of the low values of C_2F_6/I_2. Alternatively the reaction may be surface sensitive and the sulphide coating may accelerate the rate of decomposition slightly.

Choice of Another Reaction Vessel.

Because of the troubles with the nickel vessel, it was decided to instal a reactor of some other material. From the qualitative mass spectrometer analyses, it seemed that most of the CF_3 radicals reacted

with toluene in the gas phase to form CF_3H, and so only a few could reach and attack the wall. It therefore seemed unlikely that in the presence of toluene a glass or silica vessel would be attacked. The temperature was sufficiently low to enable pyrex glass to be used, so a reaction vessel of this material was constructed and installed in the existing furnace jacket.

Experiments in Pyrex Glass Reaction Vessel.

Variation of Toluene Pressure.

The experiments with the addition of toluene in the nickel vessel were not very systematic, since several variables were altered from experiment to experiment. Alexander [86] found that hydrogen iodide was produced in the reaction of toluene with iodine and no analysis had been made for this. In the following set of experiments, an attempt was made to investigate the effect of variation of toluene pressure on the reaction at constant CF_3I pressure and constant contact time. Difficulty was experienced in obtaining reproducible results and with the blocking of the spare trap. It was found necessary to "season" the reaction vessel by flowing for some time before taking readings, and the spare trap had to be modified to two traps in series to allow this to be done. The experiments in which this work was performed were not quantitative and the results are not listed.

The Reaction Products.

Iodine and benzyl iodide condensed in trap T_1 and hydrogen iodide

was found in trap T_2. Qualitative mass spectrometer analyses of the other liquid air condensable products indicated CF_3I, C_2F_6 and CF_3H. In experiment 25, the HI was not estimated and this fraction was examined on the mass spectrometer to see if any SiF_4 resulting from attack of CF_3 radicals on the glass had been produced. The main peak in the mass spectrum[93] of SiF_4 has $\frac{m}{e} = 85^+$, but no increase in this peak was found over the impurity already in the CF_3I.

As when using the nickel vessel, some white material condensed on the furnace exit tube, and it appeared once again to consist of stilbene and dibenzyl.

Table 5 contains the complete results of this series of experiments in detail. The total percentage decomposition of the CF_3I has been evaluated from the "total iodine" produced. The "total iodine" consists of the "free iodine" + benzyl iodide + hydrogen iodide. The total percentage decomposition corrected to 0.50 secs has been plotted against the toluene pressure in figure 20. In making the contact time corrections, it has been assumed that the rate is independent of contact time; this procedure cannot result in serious error since the calculated experimental contact times all lie within 4% of 0.500 secs.

FIGURE 20

PERCENTAGE DECOMPOSITION OF CF_3I IN 0·500 secs.

vs. TOLUENE PRESSURE.

797° K PYREX REACTOR.

CF_3I PRESSURE ·222 to ·239 mms.

N_2 CARRIER GAS PRESSURE 2·4 to 4·2 mms.

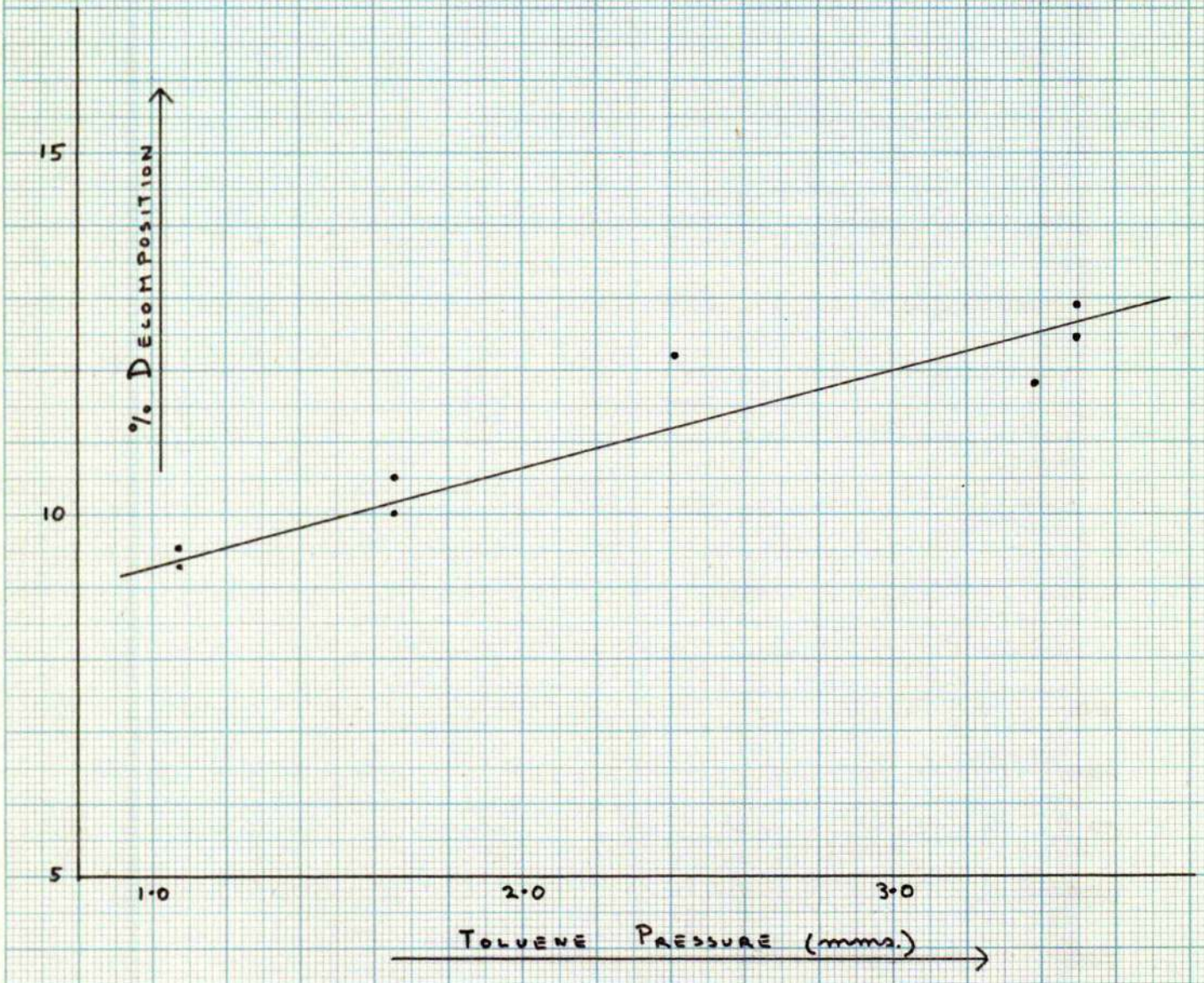


TABLE 5 Variation of Toluene Pressure

Temperature = 524°C = 797°K Nitrogen carrier gas 2.4 mms. to 4.2 mms.

Expt No.	Press CF_3I (mms)	Press. Toluene (mms)	Contact Time secs.	Moles CF_3Ix10^4 passed	Equivs I_2x10^5 formed	Moles $BzIx10^5$ formed	Moles $HIx10^5$ formed	Equivs Total I_2 $x10^5$	Total % Dec	Total % Dec at 0.50 secs.
25a	.239	1.01	.500	24.7	14.8	5.3	-			
25b	.239	1.01	.500	24.7	14.6	5.2	-			
26a	.256	1.08	.514	25.8	14.0	5.25	5.57	22.60	9.49	9.25
26b	.256	1.08	.514	25.8	14.46	4.72	4.00	23.18	9.73	9.50
27a	.226	1.66	.485	24.2	15.6	6.06	3.71	25.37	9.67	10.0
27b	.226	1.66	.485	24.2	15.9	6.01	4.84	24.75	10.20	10.5
28a	.229	2.42	.515	25.0	15.4	7.75	5.78	28.92	12.6	12.2
28b	.229	2.42	.515	25.0	15.44	7.67	5.78	28.89	12.6	12.2
29	.232	3.39	.505	25.9	15.0	9.0	6.5	28.5	11.8	11.8
30a	.222	3.49	.513	22.5	12.84	10.2	5.67	28.71	12.8	12.45
30b	.222	3.49	.515	22.5	12.84	10.4	6.54	29.78	15.2	12.9

The total percentage decomposition increases as the toluene pressure is raised. This might be due to the toluene failing to stop completely the back reaction of CF_3 radicals with iodine to reform CF_3I, but more back reaction being stopped at the higher toluene pressures. To account for the products, the reactions occurring probably include:-

$$CF_3I \longrightarrow CF_3 + I \quad (1)$$

$$I + CF_3 \longrightarrow CF_3I \quad (2)$$

$$I + I \rightleftharpoons I_2 \quad (3)$$

$$CF_3 + I_2 \longrightarrow CF_3I + I \quad (4)$$

$$CF_3 + CF_3 \longrightarrow C_2F_6 \quad (5)$$

$$CF_3 + PhCH_3 \longrightarrow CF_3H + PhCH_2 \quad (6)$$

$$2\,PhCH_2 \longrightarrow PhCH_2CH_2Ph \quad (7)$$

$$PhCH_2CH_2Ph + 2\,CF_3 \longrightarrow PhCH=CHPh + 2\,CF_3H \quad (8)$$

$$PhCH_2CH_2Ph + I_2 \longrightarrow PhCH=CHPh + 2\,HI \quad (9)$$

$$PhCH_2 + I \longrightarrow PhCH_2I \quad (10)$$

$$PhCH_2 + I_2 \longrightarrow PhCH_2I + I \quad (11)$$

$$PhCH_3 + I \longrightarrow PhCH_2 + HI \quad (12)$$

In the above scheme, Ph = the phenyl group C_6H_5

Variation of CF_3I Pressure at Constant Toluene Pressure.

The injection of toluene to pressures greater than about 4 mms. is technically difficult with the type of apparatus and technique used here. A series of experiments were therefore performed in which the pressure of CF_3I was varied at constant toluene pressure; this allowed a high $PhCH_3/CF_3I$ ratio to be achieved at reasonable toluene concentrations.

Difficulty was experienced in obtaining reproducible results at low CF_3I pressures, presumably due to the seasoning of the reaction vessel being so slow at these pressures. The technique adopted was to inject a fairly large amount of CF_3I through the two injection

capillaries in parallel for seasoning purposes and then to shut the tap controlling one capillary for performing the actual experiment. The results obtained are listed in table 6. The total percentage decompositions corrected to 0.50 secs. as before are plotted against the pressure of CF_5I in figure 21.

TABLE 6 Variation of CF_5I Pressure

Temperature = 524°C = 797°K

Nitrogen carrier gas pressure varies 3.95 to 4.36 mms.

Expt. No.	Pressure CF_5I mms.	Pressure Toluene mms.	Contact Time (secs)	Total % Dec.	Total % Dec. at 0.50 secs.
32a	.429	1.54	.467	9.9	10.6
b	.429	1.54	.467	9.7	10.4
31a	.272	1.52	.488	10.3	10.5
b	.272	1.52	.488	10.6	10.8
27a	.226	1.66	.483	9.67	10.0
b	.226	1.66	.483	10.2	10.5
33a	.173	1.61	.506	10.2	10.1
b	.175	1.61	.506	10.0	9.9
34a	.117	1.66	.475	9.1	9.6
b	.117	1.66	.475	9.1	9.6
35a	.0833	1.73	.490	8.1	8.25
b	.0833	1.73	.490	8.55	8.7
36a	.0608	1.76	.493	7.9	8.0

FIGURE 21

PERCENTAGE DECOMPOSITION OF CF_3I IN 0.500 mm. CF_3I PRESSURE

797°K PYREX REACTOR

TOLUENE PRESSURE 1.52 to 1.76 mms.

N_2 CARRIER GAS PRESSURE 3.95 to 4.36 mms.

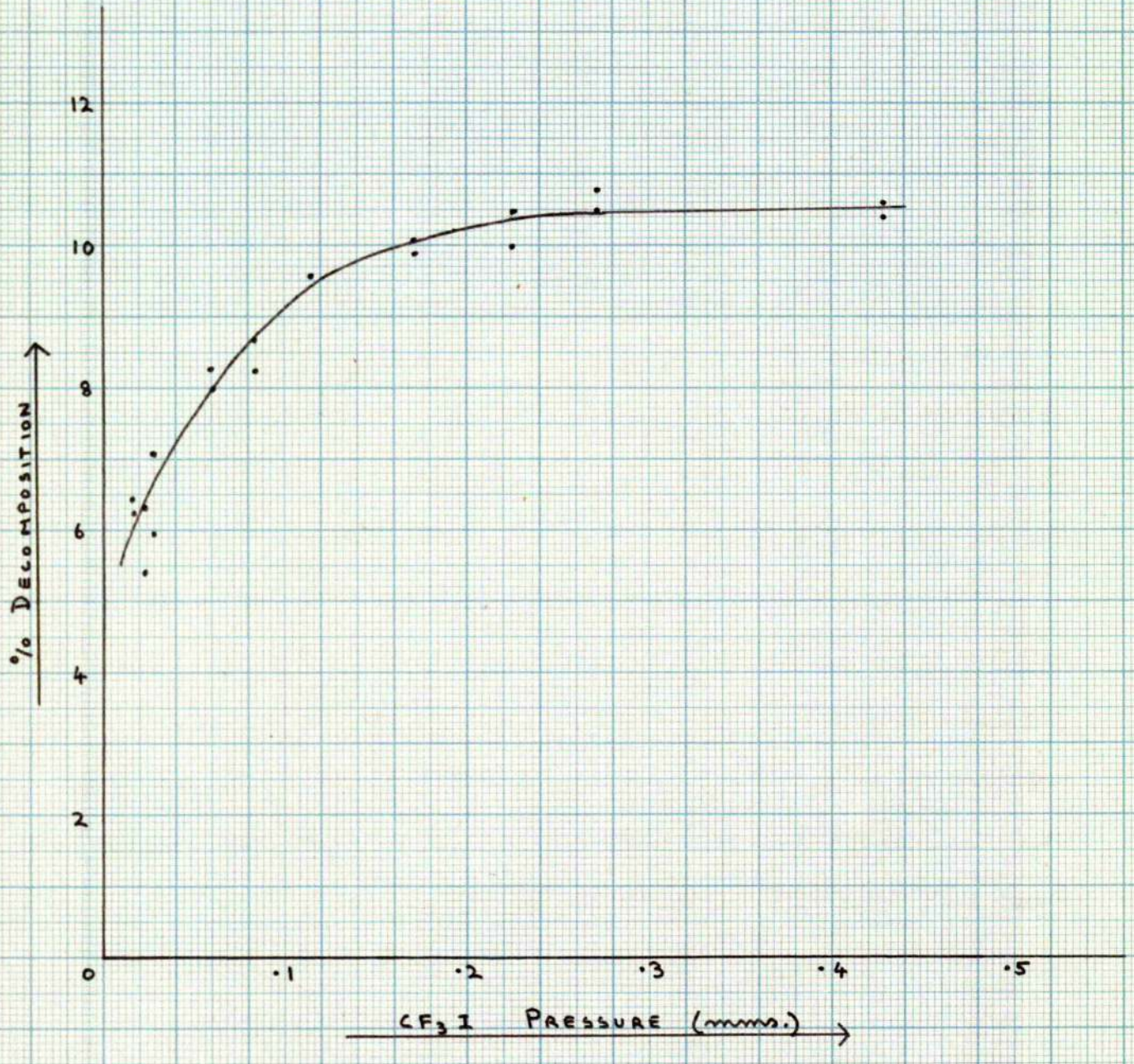


Table 6 con.

Expt. No.	Pressure CF_3I mms.	Pressure Toluene mms.	Contact Time (secs)	Total % Dec.	Total % Dec. at 0.50 secs.
56b	.0608	1.76	.495	8.2	8.3
57a	.0275	1.69	.500	5.95	5.95
b	.0275	1.69	.500	7.1	7.1
58a	.0217	1.70	.487	5.3	5.42
b	.0217	1.70	.487	6.2	6.35
59a	.0189	1.72	.505	6.3	6.25
b	.0189	1.72	.505	6.5	6.45

From figure 21, it is seen that the percentage decomposition decreases as the CF_3I pressure is lowered. This decrease cannot be due to more back reaction taking place, for there is an increase in the toluene / CF_3I ratio as the CF_3I pressure decreases.

The Hinshelwood-Lindemann theory and its more elaborate modifications predict a falling off in the rate of a reaction as the pressure of reactant is lowered. This effect has been found very markedly with CH_3I under similar pressure conditions and has been explained on this theory. It was thought that the decrease in rate found here might be due to this same reason.

To test this hypothesis, it was decided to perform a series of experiments in which the inert gas pressure was altered. If the effect suspected is the cause of the change in percentage decomposition, variation in inert gas pressure should alter the rate of reaction.

Variation of Inert Gas Pressure.

In these experiments, the pressures of CF_3I and of toluene and the contact time were kept approximately constant while the pressure of the nitrogen carrier gas was varied. The results are given in table 7, and, corrected to 0.50 seconds, are plotted in figure 22.

TABLE 7 Variation of Nitrogen Pressure

Temperature = 524°C = 797°K

Expt. No.	CF_3I Pressure (mms)	Toluene Pressure (mms)	Nitrogen Pressure (mms)	Contact Time (secs)	Percent Decomposition	Percent Decomp. at .50 secs.
43a	.231	1.68	1.50	.506	9.45	9.35
b	.231	1.68	1.50	.506	9.27	9.15
40a	.245	1.72	2.59	.496	10.6	10.7
b	.245	1.72	2.59	.496	10.7	10.8
27a	.226	1.66	4.05	.485	9.67	10.0
b	.226	1.66	4.05	.485	10.2	10.5
41a	.254	1.75	5.57	.520	11.3	10.9
b	.254	1.75	5.57	.520	11.6	11.2
42a	.261	1.53	7.85	.572	13.05	11.4

Table 7 con.

Expt. No.	CF_3I Pressure (mms)	Toluene Pressure (mms)	Nitrogen Pressure (mms)	Contact Time (secs)	Percent Decomposition	Percent Decomp. at .50 secs.
42b	.261	1.55	7.85	.572	13.55	11.7
45a	.220	1.61	9.87	.475	11.45	11.9
b	.220	1.61	9.87	.475	11.9	12.4
44a	.249	1.96	12.3	.558	13.7	12.3
b	.249	1.96	12.3	.588	13.9	12.3

A small increase in rate as the nitrogen pressure was raised was found, the increase being about 20% for a rise in nitrogen pressure of 14 mms.

These experiments had been performed at a CF_3I pressure where the rate did not alter rapidly with change in CF_3I concentration, and it was thought that a more marked effect might be obtained when the pressure of CF_3I was lower. Accordingly, another set of experiments were performed at a CF_3I pressure of about .09 mms. These results, corrected to 0.50 secs. are also plotted in figure 22 and are listed in table 8.

TABLE 8 Variation of Nitrogen Pressure

Temperature = 524°C = 797°K

Expt. No.	CF_3I Pressure (mms)	Toluene Pressure (mms)	Nitrogen Pressure (mms)	Contact Time (secs)	Total % Decomp.	Total % Dec at .50 secs.
46a	.092	1.79	1.56	.520	8.0	7.7
b	.092	1.79	1.56	.520	8.2	7.9
35a	.083	1.73	4.12	.490	8.1	8.25
b	.083	1.73	4.12	.490	8.55	8.7
48a	.0845	1.71	8.05	.497	9.55	9.6
b	.0845	1.71	8.05	.497	9.70	9.75
47a	.084	1.67	15.5	.486	9.6	9.9
b	.084	1.67	15.5	.486	9.0	9.5

These results lie on a line substantially parallel to the line at higher CF_3I pressure. It was feared that these results might be due to some systematic error of the flow system. To check this, a series of experiments were carried out where argon was used as carrier gas and its pressure varied. These experiments with the argon carrier gas were carried out at the higher pressure of CF_3I as more data were available there. The results have been plotted on the same graph as the results for nitrogen (figure 22) and are listed in table 9.

FIGURE 22

PERCENTAGE DECOMPOSITION OF CF_3I IN 0·500 mms. vs. INERT GAS PRESSURE AT 797°K

= VARIATION OF N_2 PRESSURE WITH ·226 to ·261 mms. CF_3I

= VARIATION OF N_2 PRESSURE WITH ·083 to ·092 mms. CF_3I

= VARIATION OF ARGON PRESSURE WITH ·235 to ·250 mms. CF_3I

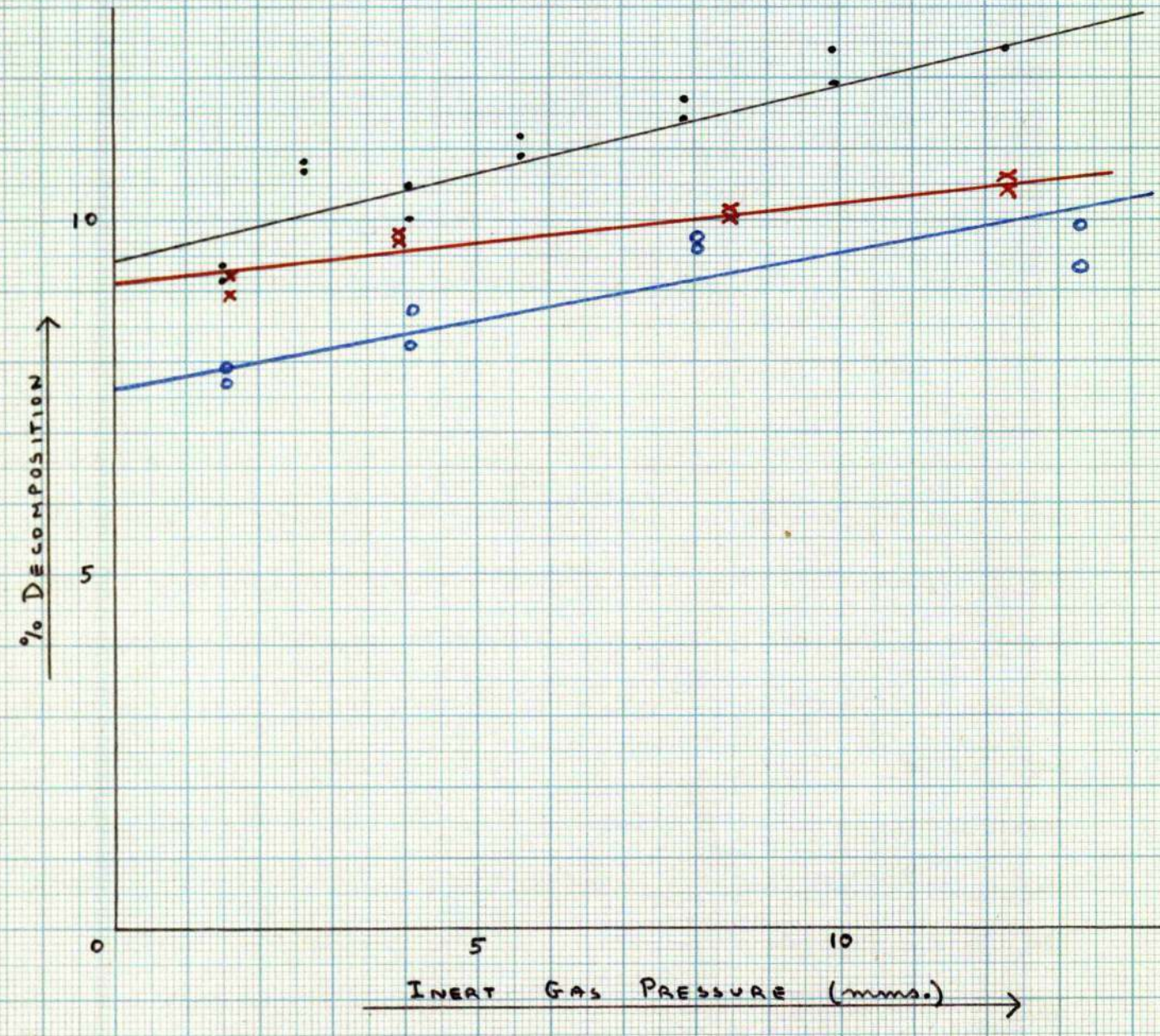


TABLE 9 Variation of Argon Pressure

Temperature = 524°C = 797°K

Expt. No.	CF_3I Pressure (mms)	Toluene Pressure (mms)	Argon Pressure (mms)	Contact Time (secs)	Total % Decomp	Total % Dec at .50 secs
49a	.247	1.82	1.59	.550	9.76	9.2
b	.247	1.82	1.59	.550	9.45	8.9
51a	.250	1.85	5.96	.550	10.65	9.7
b	.250	1.85	5.96	.550	10.75	9.8
50a	.255	1.65	8.47	.505	10.1	10.0
b	.255	1.65	8.47	.505	10.25	10.15
52a	.245	1.72	12.5	.510	10.8	10.6
b	.245	1.72	12.5	.510	10.6	10.4

It is seen that the slope of this line is less than the slopes of the lines obtained in the alteration of nitrogen pressure and that the difference in slopes is outside the experimental error. Argon would be anticipated to be less efficient than nitrogen in transferring energy, so the results obtained are in line with theoretical expectation. Extrapolation of the data obtained with nitrogen and argon at approximately 0.24 mms. CF_3I yields almost the same intercept on the percentage decomposition axis for both series of experiments. This is the decomposition produced in 0.24 mms. CF_3I in 1.7 mms. toluene with no other gas present. It was considered that the

apparently small effect of both gases might be due to the reaction still being slightly inhibited and to the large pressure of toluene which would itself transfer energy to the CF_3I.

Mass Spectrometric Estimation of CF_3H and C_2F_6.

A supply of C_2F_6 - CF_4 mixture had by this time been given to us by I.C.I. and separation of these compounds provided us with mass spectrometric standards for analysis; this enabled us to investigate the production of CF_3H and C_2F_6 at different toluene concentrations. A nitrogen pressure of about 8 mms was used in the hope that it might be possible to attain conditions where the reaction was more nearly first order in CF_3I. The analytical procedure has already been described (page 51). The results are listed in table 10.

FIGURE 23

PERCENTAGE DECOMPOSITION OF CF_3I IN 0·500 mms.

vs. TOLUENE PRESSURE.

797°K

CF_3I PRESSURE = ·224 to ·237 mms.

N_2 CARRIER GAS PRESSURE 7·6 to 8·2 mms.

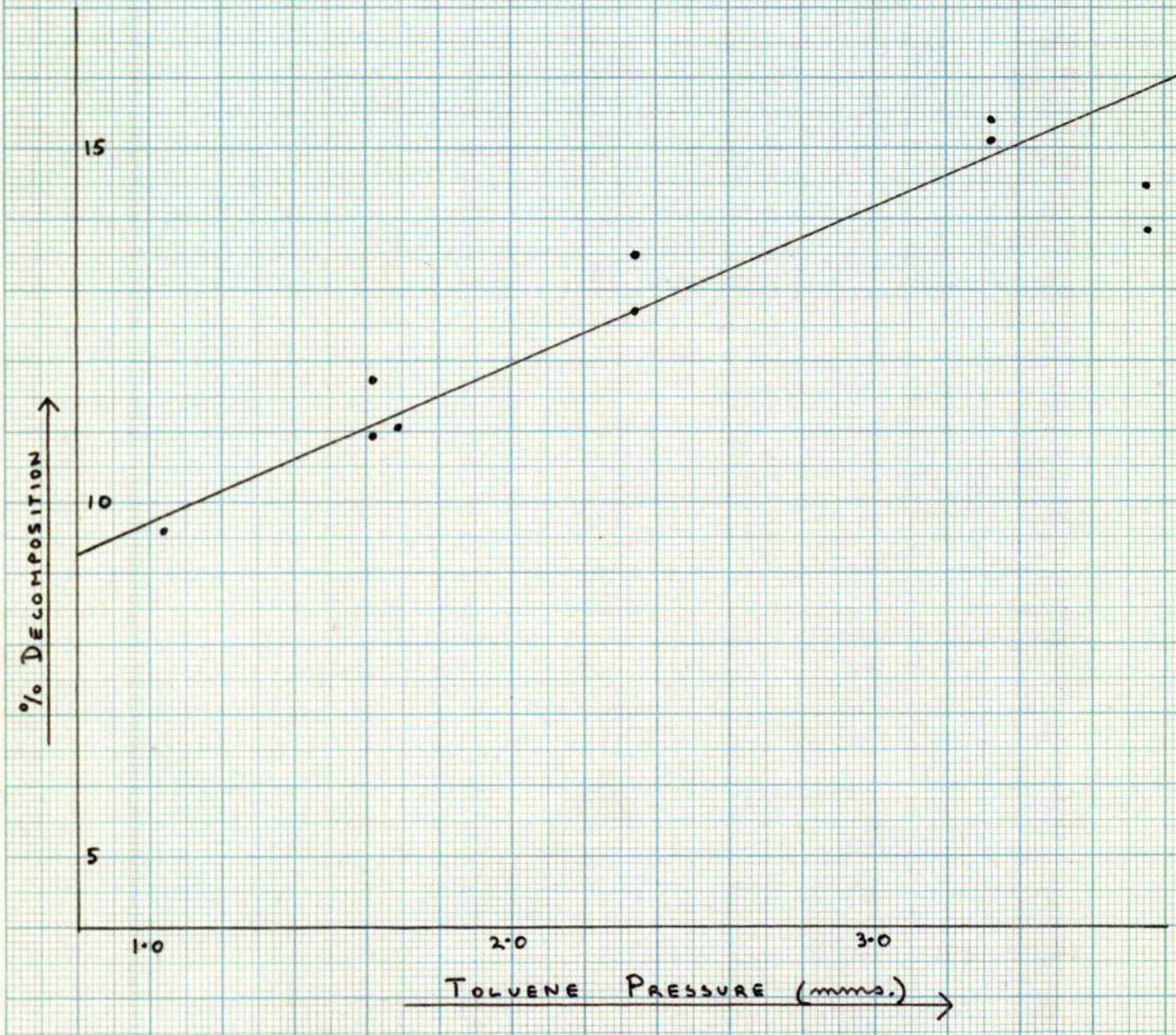


TABLE 10 Variation of Toluene Pressure with Estimation of CF_3H and C_2F_6

Temperature = 524°C = 797°K

Nitrogen Pressure = 7.6 to 8.2 mms.

Expt. No.	Pressure CF_3I (mms)	Pressure Toluene (mms)	Contact Time (secs)	Total % Dec	Total % Dec at.50 secs.	Equivs "Total I" $x10^5$	Moles CF_3H $x10^5$
53a	.224	1.04	.501	9.6	9.6	22.1	14.2
b				9.6	9.6	22.1	15.2
54a	.225	1.69	.493	10.95	11.1	18.9	14.1
b				10.95	11.1	18.9	13.7
58a	.224	1.62	.495	10.8	10.95	18.9	14.4
b				11.6	11.75	20.45	15.4
55a	.236	2.35	.484	12.3	12.7	23.45	15.4
b				15.1	15.5	25.05	17.3
56a	.237	3.33	.526	15.9	15.1	18.6	14.4
b				16.2	15.4	19.0	13.7
57a	.232	3.76	.508	14.4	14.2	13.8	12.6
b				15.1	14.9	14.45	11.8

Table 10 Continued:

Expt. No.	Moles C_2F_6 $x\ 10^5$	$\frac{2 \times \text{moles} C_2F_6}{\text{moles } CF_3H}$	$\frac{\text{Total "}CF_3\text{"}}{\text{Total I}}$	$R(CF_3H)$ $x\ 10^7$	$R(C_2F_6)$ $x\ 10^8$	$\frac{R(CF_3H)}{[R(C_2F_6)]^{\frac{1}{2}}}$ $x\ 10^3$	Toluene Concn. $x\ 10^5$ moles/l
53a	1.11	15.6%	.745	5.52	4.32	2.65	2.09
b	1.03	13.6%	.785	5.90	4.00	2.85	
54a	.65	9.2%	.815	7.30	3.46	3.93	3.40
b	.58	8.5%	.785	7.10	3.00	4.08	

FIGURE 24

$\frac{2\times \text{MOLES } C_2F_6 \text{ FORMED}}{\text{MOLES } CF_3H \text{ FORMED}}$ (PERCENTAGE) vs. TOLUENE PRESSURE

797°K

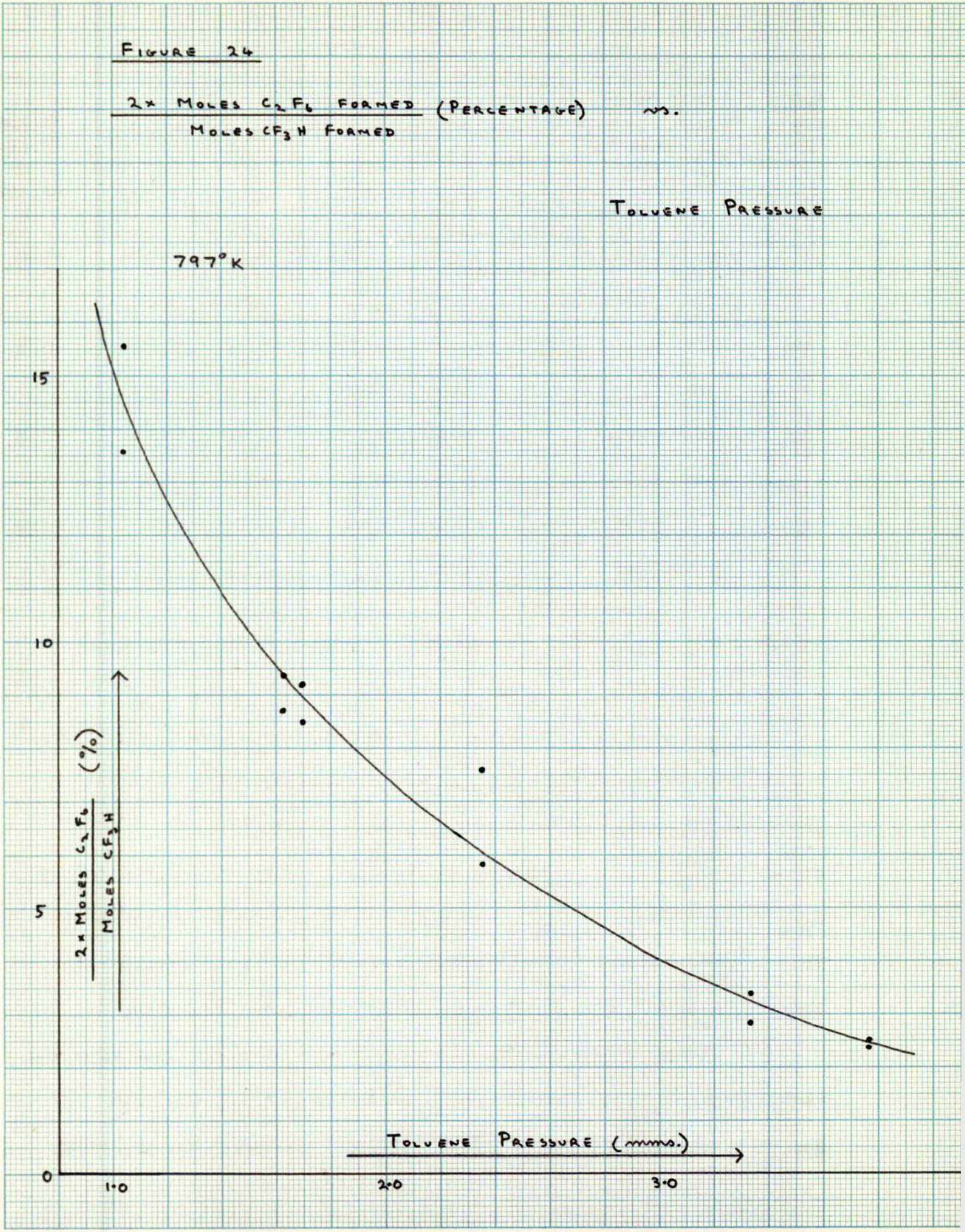


Table 10 Continued:

Expt. No.	Moles C_2F_6 x 10^5	2 x moles C_2F_6 / moles CF_3H	Total "CF_3" / Total I	$R(CF_3H)$ x 10^7	$R(C_2F_6)$ x 10^8	$\frac{R(CF_3H)}{[R(C_2F_6)]^{\frac{1}{2}}}$ x 10^3	Toluene Concn. x 10^5 moles/l
58a	.68	9.4%	.84	7.45	5.52	5.95	5.26
b	.67	8.7%	.82	7.97	5.48	4.25	
55a	.585	7.6%	.71	7.98	5.05	4.58	4.75
b	.506	5.85%	.75	8.98	2.62	5.54	
56a	.240	5.3%	.80	11.2	1.87	8.18	6.70
b	.195	2.85%	.74	10.7	1.55	8.64	
57a	.14	2.4%	.94	12.3	1.41	10.3	7.56
b	.15	2.5%	.85	11.5	1.46	9.5	

In table 10, "total CF_3" = moles CF_3H + 2 (moles C_2F_6) recovered.

$R(CF_3H)$ = rate of formation of CF_3H in moles $l^{-1}sec^{-1}$

$R(C_2F_6)$ = rate of formation of C_2F_6 in moles $l^{-1}sec^{-1}$

Figure 23 shows that the percentage decomposition, corrected to .50 secs, increases with toluene pressure as found before. The column headed "2 x C_2F_6/CF_3H" represents the ratio of "CF_3" found in C_2F_6 to that found in CF_3H. It has been expressed as a percentage. This ratio decreases as the toluene pressure is raised (figure 24); this is in agreement with the previously postulated mechanism.

For all experiments, the "total CF_3" recovered was less than the "total iodine" found. In experiments 56, 57 and 58, the mass spectrometer was calibrated while actually performing the analysis,

but the mass balance was no better in these cases. Recovery of CF_3H from the apparatus appeared to be quantitative to within ± 5% under a simulation of experimental conditions and it did not dissolve in toluene to any extent at -80°C at the pressures used.

Ayscough and Steacie [56] have proposed that reactions of the type

$$C F_3 + R \longrightarrow C F_3 R$$

occur when hexafluoroacetone is photolyzed in the presence of hydrocarbons. They found and estimated the compound $CF_3 CH_3$ in experiments using methane. It is therefore not impossible that the reaction

$$C F_3 + C_6 H_5 C H_2 \longrightarrow C_6 H_5 C H_2 C F_3$$

might have occurred. Trotman-Dickenson[42] considers that the reaction

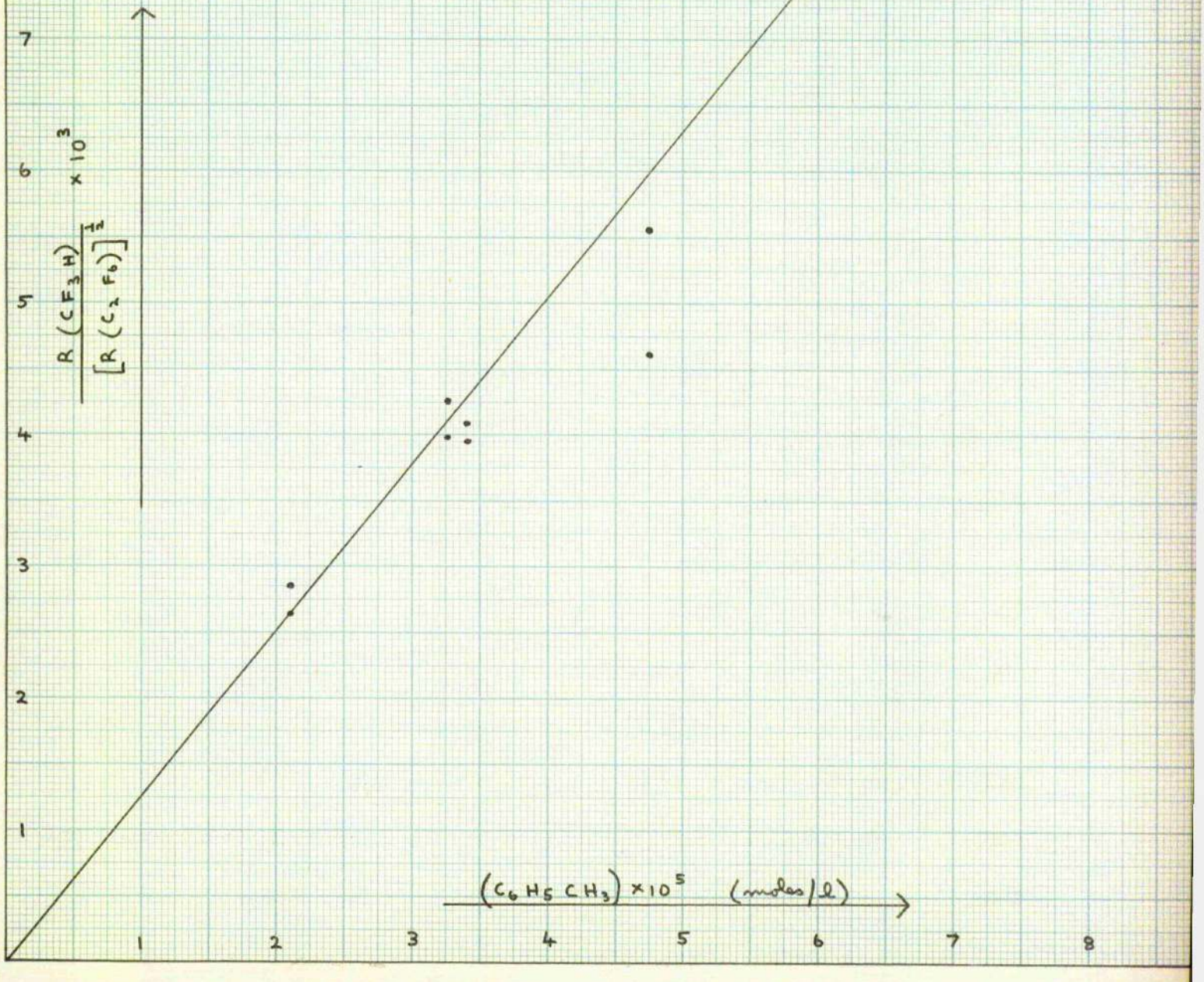
$$C H_3 + C_6 H_5 C H_2 \longrightarrow C_6 H_5 C H_2 C H_3$$

is probable and will have an activation energy of 1 ± 4 K cals./mole. A search using the mass spectrometer was therefore made in the products collected in traps T_1 and T_2 for the parent peak of $C_6H_5CH_2CF_3$. Nothing was found, but since any material of this type would probably condense in trap 1 at -80°, its detection and estimation among the large quantity of toluene present would be very difficult. The ratio "total CF_3" / "total iodine" does not appear to depend on the toluene concentration; this is in agreement with the formation of $C_6H_5CH_2CF_3$ for its rate of production depends on the concentration of benzyl radicals and not on the toluene pressure. The low amount of "CF_3" recovered might be due to some systematic analysis error but none was

FIGURE 25

$\frac{R(CF_3H)}{[R(C_2F_6)]^{\frac{1}{2}}}$ vs. TOLUENE CONCENTRATION AT 797°K

R(X) = RATE OF FORMATION OF X IN moles. l^{-1}. sec^{-1}.



detected.

If the CF_3H formed results only from attack of CF_3 radicals on toluene

$$CF_3 + PhCH_3 \longrightarrow CF_3H + PhCH_2 \qquad (6)$$

and if the C_2F_6 is formed only from dimerization of CF_3 radicals

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (5),$$

the following equations may be written:-

$$R(CF_3H) = k_6 (CF_3)(PhCH_3)$$

$$R(C_2F_6) = k_5 (CF_3)^2$$

where R (x) = rate of formation of x.

Then, $$\frac{R(CF_3H)}{R\left[(C_2F_6)\right]^{\frac{1}{2}}} = \frac{k_6 (CF_3)(PhCH_3)}{(k_5)^{\frac{1}{2}} (CF_3)}$$

$$= \frac{k_6}{(k_5)^{\frac{1}{2}}} (PhCH_3)$$

Therefore a plot of $\frac{R(CF_3H)}{R\left[(C_2F_6)\right]^{\frac{1}{2}}}$ against the concentration of toluene should give a straight line through the origin of slope = $k_6 / (k_5)^{\frac{1}{2}}$.

Figure 25 shows that this is in fact the case and gives support to the mechanism proposed. From the graph,

$k_6 / (k_5)^{\frac{1}{2}} = 128\ l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ secs^{-\frac{1}{2}}$ at 797°K.

This set of experiments has confirmed the explanation of the results already put forward, and the gas analyses have shown conclusively that all the CF_3 radicals do not react with toluene, and that back reaction must still occur.

The Products of the Reaction between Toluene and Iodine.

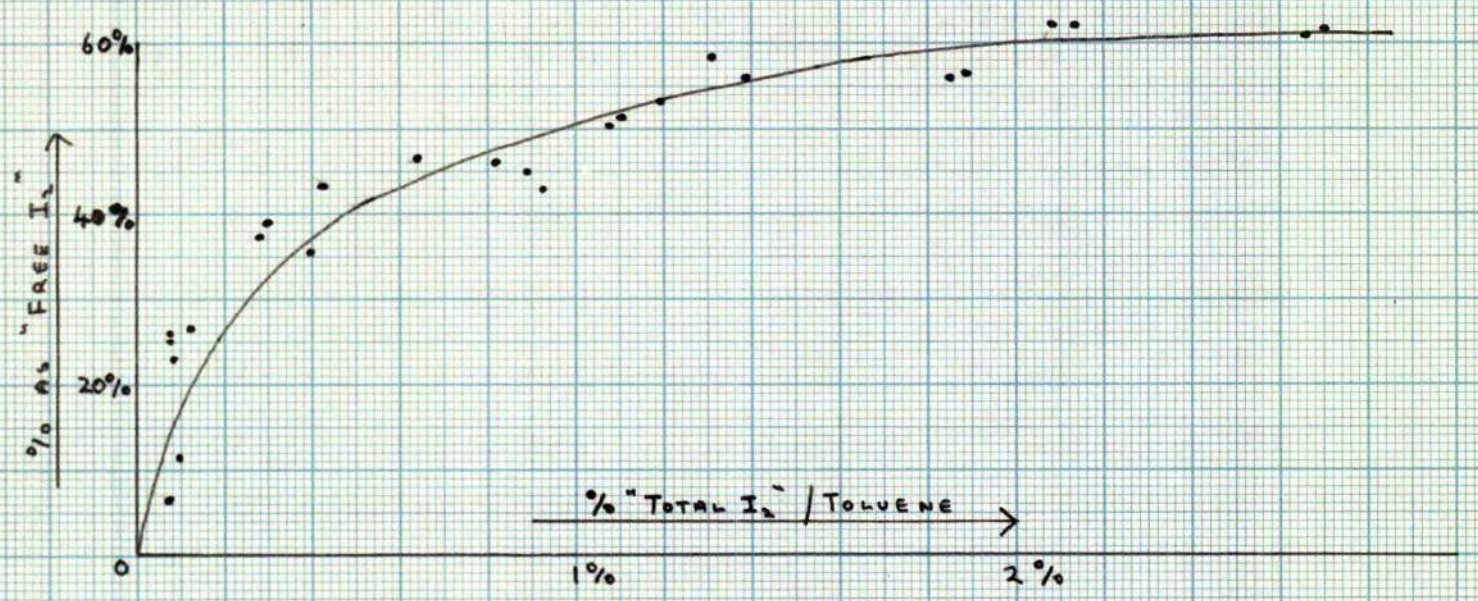
In all the foregoing work with toluene, most of the emphasis has been laid on the "total iodine" produced, since only the "total iodine" is of interest from the point of view of the decomposition of CF_5I. However, the data obtained have given information on the extent of formation of the different products as the toluene to iodine ratio has been altered, and these results are of intrinsic interest. The "total iodine" consists of the "free iodine" + benzyl iodide + hydrogen iodide and in table 11 are listed the data for experiments 26 to 39 on the variation of the proportions of these products with altering "total iodine" / toluene ratio. Experiments 26 to 39 were the first to be carried out with toluene in the pyrex reaction vessel; they cover the limits of the "total iodine" / toluene ratio achieved in this work and show the trend of the variations.

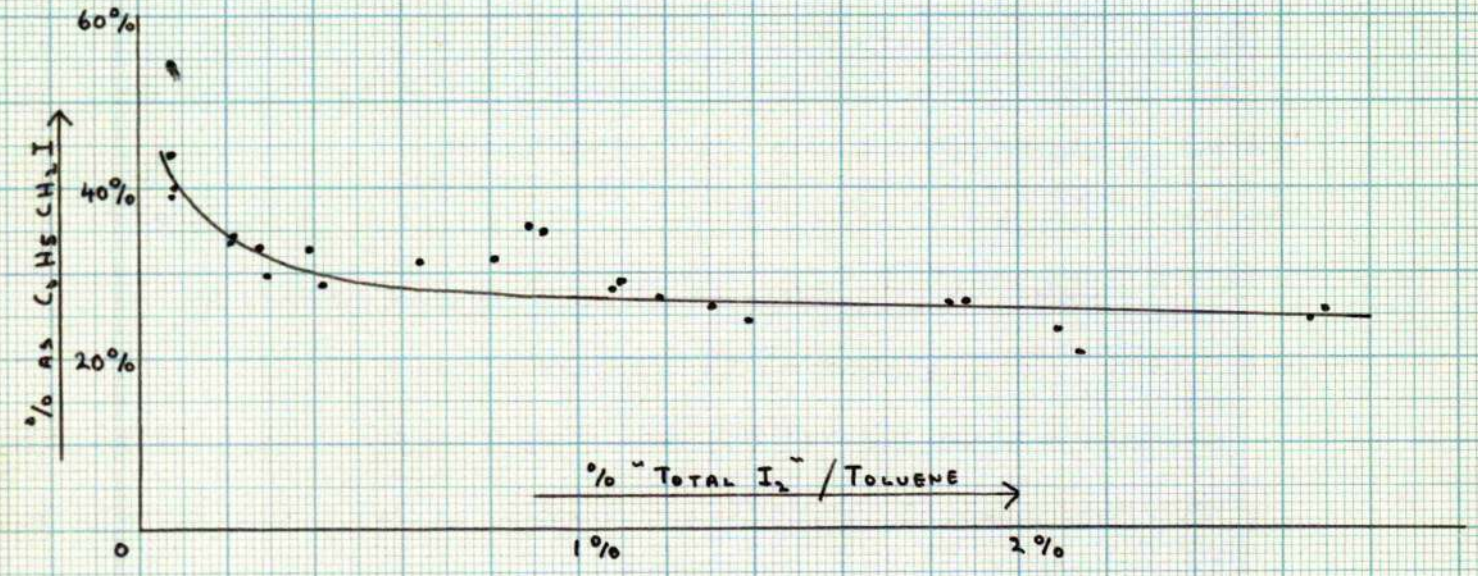
TABLE 11.

Production of "Free Iodine", Benzyl Iodide, and Hydrogen Iodide at Different "Total Iodine" / Toluene ratios. 797°K Contact Time .467 to .515 secs.

Expt. No.	% of Total Iodine as Free Iodine	% of Total Iodine as BzI	% of Total Iodine as HI	Total Iodine / Toluene (Percentage)
26a	62.0	25.2	14.9	2.09
b	62.0	20.4	17.5	2.14
27a	58.0	25.9	15.9	1.51
b	56.2	24.5	19.5	1.59
28a	55.2	26.8	20.3	1.19
b	55.2	26.8	20.3	1.19
29	46.0	31.6	22.3	.81
30a	44.7	35.5	19.8	.89
b	43.0	34.9	21.9	.925
32a	61.5	25.9	13.8	2.7
b	60.9	24.6	14.4	2.66
31a	56.0	26.5	17.4	1.85
b	56.5	26.5	17.1	1.89
33a	51.3	29.1	19.5	1.10
b	50.4	28.1	21.4	1.08
34a	46.4	31.2	22.3	.635
b	46.4	30.7	22.9	.635
35a	35.5	32.7	29.9	.595
b	45.3	28.4	28.7	.417

FIGURE 26 PRODUCTION OF "FREE I_2", BENZYL IODIDE AND HYDROGEN IODIDE AS IODINE / TOLUENE VARIES AT 797°K





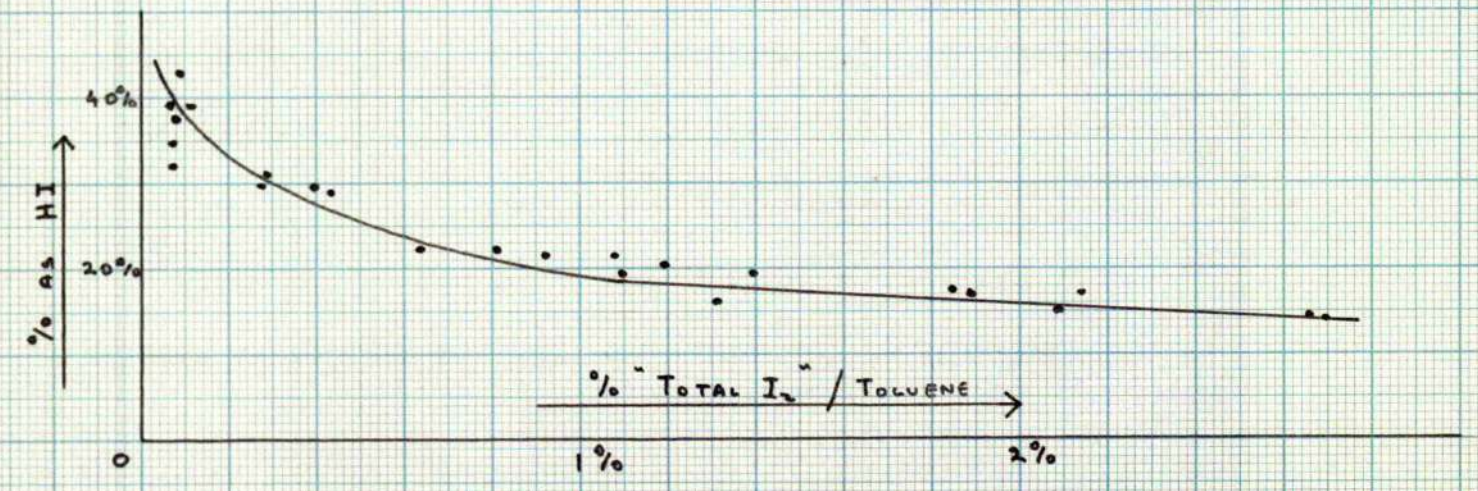


Table 11 con.

Expt. No.	% of Total Iodine as Free Iodine	% of Total Iodine as BzI	% of Total Iodine as HI	Total Iodine / Toluene (Percentage)
36a	37.0	33.1	29.8	.276
b	38.8	29.9	31.2	.288
37a	11.5	45.5	43.0	.0965
b	26.5	34.4	39.1	.116
38a	6.5	54.5	38.9	.068
b	22.3	40.0	37.6	.079
39a	25.0	44.0	32.2	.069
b	25.7	39.5	34.7	.071

BzI in the above table represents benzyl iodide.

The "total iodine" / toluene is the total iodine as equivalents produced divided by the number of moles of toluene passed in the experiment. It is expressed as a percentage.

In figure 26 is plotted the data listed in table 11. It is seen that the percentage of free iodine increases as the iodine to toluene ratio increases. This is in agreement with expectation.

The percentage of HI increases as the "total iodine" / toluene ratio decreases. This is once again the result that might be expected, for HI is produced by the reaction

$$I + Ph\,C\,H_3 \longrightarrow Ph\,C\,H_2 + HI \qquad (12)$$

The formation of benzyl iodide at this temperature is rather

surprising. The temperature dependence of the rate constant $\underline{k}$ for the reaction

$$Bz\ I \longrightarrow Bz + I$$

is given approximately by

$$k = 10^{15} \exp(-45{,}000/RT)$$

Therefore at $800^{\circ}k$

$$\log k = 15 - 11.75 = 1.25$$

$$k = 18\ secs^{-1}$$

Hence the half life = $\frac{.69}{18} = \underline{3.8.10^{-2}\ secs.}$

Thus it might be expected that it would not be produced in any quantity under the experimental conditions. However, the formation of benzyl iodide can occur by the processes

$$Bz + I \longrightarrow Bz\ I \qquad (10)$$

and $$Bz + I_2 \longrightarrow Bz\ I + I \qquad (11)$$

Benzyl radicals are fairly stable and may not react in the hot zone, so it is possible that reactions (10) and (11) take place in the exit from the reaction vessel. A slight increase in the proportion of benzyl iodide as the iodine/toluene ratio is lowered might then reasonably be expected, for under these conditions relatively more benzyl radicals are formed by reaction (12)

$$I + Ph\ CH_3 \longrightarrow Ph\ CH_2 + HI \qquad (12)$$

These results would suggest that toluene is not a very suitable "catcher" for radicals in a system containing iodine because of the complex secondary reactions which occur.

Addition of Hydrogen Iodide.

Toluene is recognised as a good "catcher" of radicals in the gas phase, probably mainly due to the work of Szwarc using the "toluene carrier gas" technique. Nevertheless, the continued formation of C_2F_6 indicated that the toluene was not removing CF_3 radicals completely to form CF_3H. There must have been a sufficiently high concentration of CF_3 radicals in the system to permit the occurrence of the reaction

$$C F_3 + C F_3 \longrightarrow C_2 F_6 \qquad (5)$$

The concentration of iodine in the system must have been higher than the concentration of CF_3 radicals so the reactions

$$C F_3 + I \longrightarrow C F_3 I \qquad (2)$$

and $$C F_3 + I_2 \longrightarrow C F_3 I + I \qquad (4)$$

probably also occurred.

It was therefore decided to try to capture $C F_3$ radicals in some other manner. Hydrogen iodide has been used a little as a radical catcher but has not received the attention accorded to nitric oxide, propylene or toluene.

Iredale and Stephan[18] photolyzed mixtures of CH_3I and HI and found a quantum yield of 2 for mixtures containing from 40% to 88% of HI. They attributed this to the reactions

$$C H_3 I + h\nu \longrightarrow C H_3 + I$$

$$C H_3 + H I \longrightarrow C H_4 + I$$

All the methyl radicals reacted with the HI when the concentration of

the latter was sufficiently high.

Ogg[38] has employed HI in investigations of the pyrolyses of methyl, ethyl and n-propyl iodides. He considered that a bimolecular reaction

$$R\,I + H\,I \longrightarrow R\,H + I_2$$

occurred as well as the reaction

$$R + HI \longrightarrow R\,H + I$$

More recently, Alexander[86] has used HI to react with benzyl radicals formed in the pyrolysis of dibenzyl.

The bond energy D (H-I) = 71 K cals/mole[45,44] so it might be expected that the energy of activation for the reaction

$$C\,F_3 + HI \longrightarrow C\,F_3\,H + I \qquad (15)$$

would be less than for reaction (6)

$$C\,F_3 + Ph\,C\,H_3 \longrightarrow Ph\,C\,H_2 + C\,F_3\,H \qquad (6)$$

since the lowest estimate of D ($PhCH_2$-H) is 77.5 K cals/mole.[94] Therefore it would appear that HI will probably be better than toluene as a "catcher" of CF_3 radicals.

<u>The Possible Decomposition of HI under Reaction Conditions.</u>

Hydrogen iodide decomposes by a bimolecular mechanism according to

$$\frac{d\,(I_2)}{dt} = \frac{d\,(H_2)}{dt} = k\,(HI)(HI)$$

The temperature dependence of <u>k</u> is given by

$$k = 10^{10.9} \exp\,(-44{,}000/RT)\ 1.mole^{-1}\ sec^{-1}.$$

Now it is clearly undesirable to consider HI as a radical acceptor at temperatures where its own decomposition to give iodine would be a prominent contribution to the total yield. If, under our kinetic flow system conditions, the maximum premissible rate of formation of iodine from HI is taken to be 10^{-9} moles. $l.^{-1}$ $sec.^{-1}$, which is about 0.2% of the rate of formation of iodine in most of the experiments with toluene, we have at 797°K,

$$\frac{d(I_2)}{dt} = k\,(HI)^2$$

$$10^{-9} = 10^{10.9} \cdot 10^{-12}\,(HI)^2$$

or $(HI) = 10^{-5.95} = 1.1.10^{-4}$ moles/l

$= \underline{5.6 \text{ mms. HI.}}$

Thus it should be possible to inject up to 5 mms. HI before the rate of decomposition becomes appreciable.

Experiments using Hydrogen Iodide.

The Products of the Reaction.

The products were examined carefully in a few experiments in the course of which a suitable temperature at which to investigate the effect of HI pressure was found.

The only product found condensed in trap T_1 was iodine. Mass spectrometer analysis of the liquid air condensable products by the technique already described (p 51) revealed only unchanged CF_3I and CF_3H together with a little HI unremoved by the NaOH solution. No C_2F_6 was found. Quantitative analysis was made for the CF_3H on the

mass spectrometer, the sensitivity being found by injecting CF_5H into the actual analysis sample. These results are listed in table 12.

TABLE 12 The Products of the Reaction with HI.
Pressure of N_2 carrier gas = 4.40 to 4.74 mms.

Expt. No.	Tempr (^oK)	Pressure CF_5I (mms)	Pressure HI (mms)	Contact Time secs	Percent Decomp	Moles $I_2 \times 10^5$ formed	Moles $CF_5H \times 10^5$ formed	Moles CF_5H / Moles I_2
59a	797	.230	1.19	.497	27.5	52.9	32.0	.97
b	797	.230	1.19	.497	27.5	52.9	57.0	1.12
60a	774	.240	1.10	.556	12.25	14.8	12.6	.85
b	774	.240	1.10	.556	15.4	16.25	-	-
61a	758	.234	1.08	.530	6.75	8.1	6.75	.83
b	758	.234	1.08	.530	7.05	8.45	7.15	.85
62a	758	.224	1.53	.506	5.45	5.25	5.1	.97
b	758	.224	1.53	.506	5.7	5.5	5.85	1.06
63a	758	.225	.715	.514	4.7	4.44	4.3	.97
b	758	.225	.715	.514	5.1	4.78	5.1	1.06

The absence of C_2F_6 suggested that HI was much more efficient in reacting with CF_3 radicals than was toluene. The large decomposition found in expt. 59 confirmed this and the temperature was lowered about 40 C^o to give more suitable percentage decompositions. The ratio moles CF_5H / moles I_2 varies from .83 to 1.12, which would indicate

that, within the rather large analysis error, the stoichiometric equation is

$$C F_3 I + H I \longrightarrow C F_3 H + I_2$$

All the CF_3 radicals would appear to react by the process

$$C F_3 + H I \longrightarrow C F_3 H + I \qquad (15)$$

The dimerisation of radicals must therefore have been stopped, and probably the back reaction to reform trifluoromethyl iodide was prevented or greatly reduced.

Variation of Pressure of HI.

A systematic variation of HI pressure was carried out while trying to keep the pressure of CF_3I and the contact time constant. This was investigated fairly thoroughly as it was feared that there might be a bimolecular reaction

$$C F_3 I + H I \longrightarrow C F_3 H + I_2$$

similar to the type claimed by Ogg[38]. Table 13 lists the results and they are plotted, corrected to 0.500 secs in figure 27a.

TABLE 13 Variation of HI Pressure

Temperature = 485°C = 758°K

N_2 carrier gas pressure = 3.64 to 4.77 mms.

Decomposition calculated from iodine produced.

Expt. No.	CF_3I Pressure (mms)	HI Pressure (mms)	Contact Time (secs)	Percent Decomp.	Percent Decomp at .50 secs.	% Dec at .50 secs at .24 mms.
73a	.250	.051	.566	2.58	2.28	2.19
b	.250	.051	.566	2.9	2.55	2.45
c	.250	.051	.566	2.54	2.25	2.16
72a	.244	.072	.554	4.08	3.6	3.55
b	.244	.072	.554	3.5	3.0	2.95
c	.244	.072	.554	3.6	3.25	3.20
71a	.241	.131	.544	4.47	4.1	4.1
b	.241	.131	.544	4.8	4.45	4.45
c	.241	.131	.544	4.3	3.95	3.95
70a	.247	.476	.540	6.3	5.8	5.65
b	.247	.476	.540	6.7	6.2	6.0
c	.247	.476	.540	6.55	6.15	5.0
63a	.225	.715	.514	4.7	4.6	4.95
b	.225	.715	.514	5.1	4.95	5.35
66a	.244	1.01	.534	6.8	6.3	6.2
b	.244	1.01	.534	7.2	6.7	6.6

Table 15 Con.

Expt. No.	CF_3I Pressure (mms)	HI Pressure (mms)	Contact Time (secs)	Percent Decomp.	Percent Decomp at .50 secs.	% Dec at .50 secs at .24 mms.
66c	.244	1.01	.554	6.65	6.2	6.1
61a	.254	1.08	.530	6.75	6.35	6.5
b	.254	1.08	.530	7.05	6.65	6.8
62a	.224	1.53	.506	5.45	5.4	5.8
b	.224	1.53	.506	5.7	5.65	6.1
67	.248	1.84	.550	7.2	6.55	6.35
64a	.256	1.97	.559	6.7	5.95	6.05
b	.256	1.97	.559	7.3	6.5	6.6
68a	.241	2.08	.526	7.5	7.1	7.1
b	.241	2.08	.526	7.7	7.3	7.5
c	.241	2.08	.526	7.0	6.65	6.65
65a	.254	2.50	.581	7.95	6.85	6.5
b	.254	2.50	.581	8.4	7.2	6.8
c	.254	2.50	.581	7.7	6.65	6.3
69a	.250	4.08	.511	7.45	7.3	7.6
b	.257	3.72	.570	7.8	6.9	6.45
c	.257	3.72	.570	7.4	6.5	6.05

In the final column of table 15, the results have been corrected to 0.24 mms. CF_3I assuming that the reaction is second order in CF_3I; these corrected results have been plotted in figure 27b and give a less

FIGURE 27a HI PRESSURE vs. PERCENTAGE DECOMPOSITION OF CF_3I CORRECTED TO 0·500 secs. CONTACT TIME 758°K

CF_3I PRESSURE VARIES ·222 to ·257 mms.

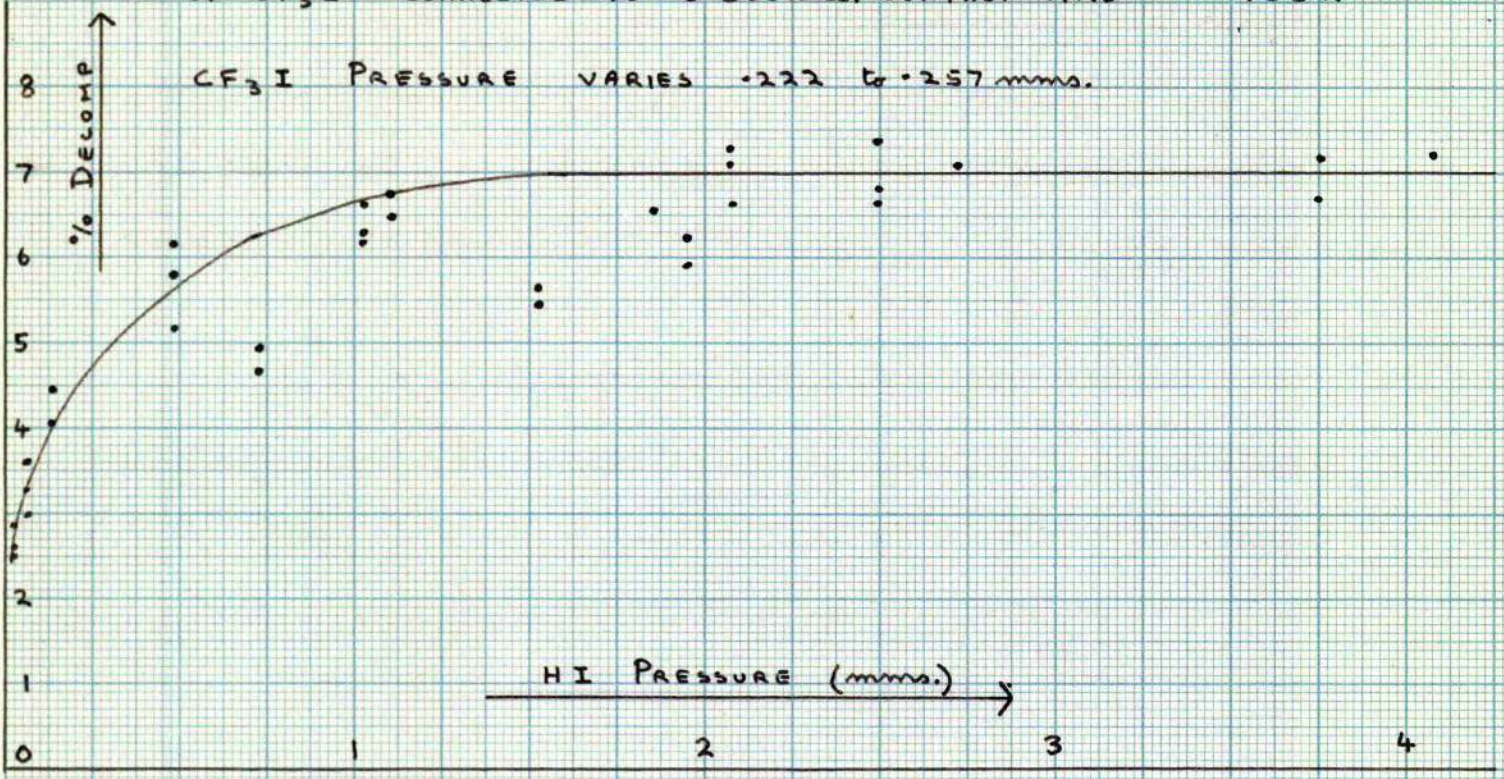
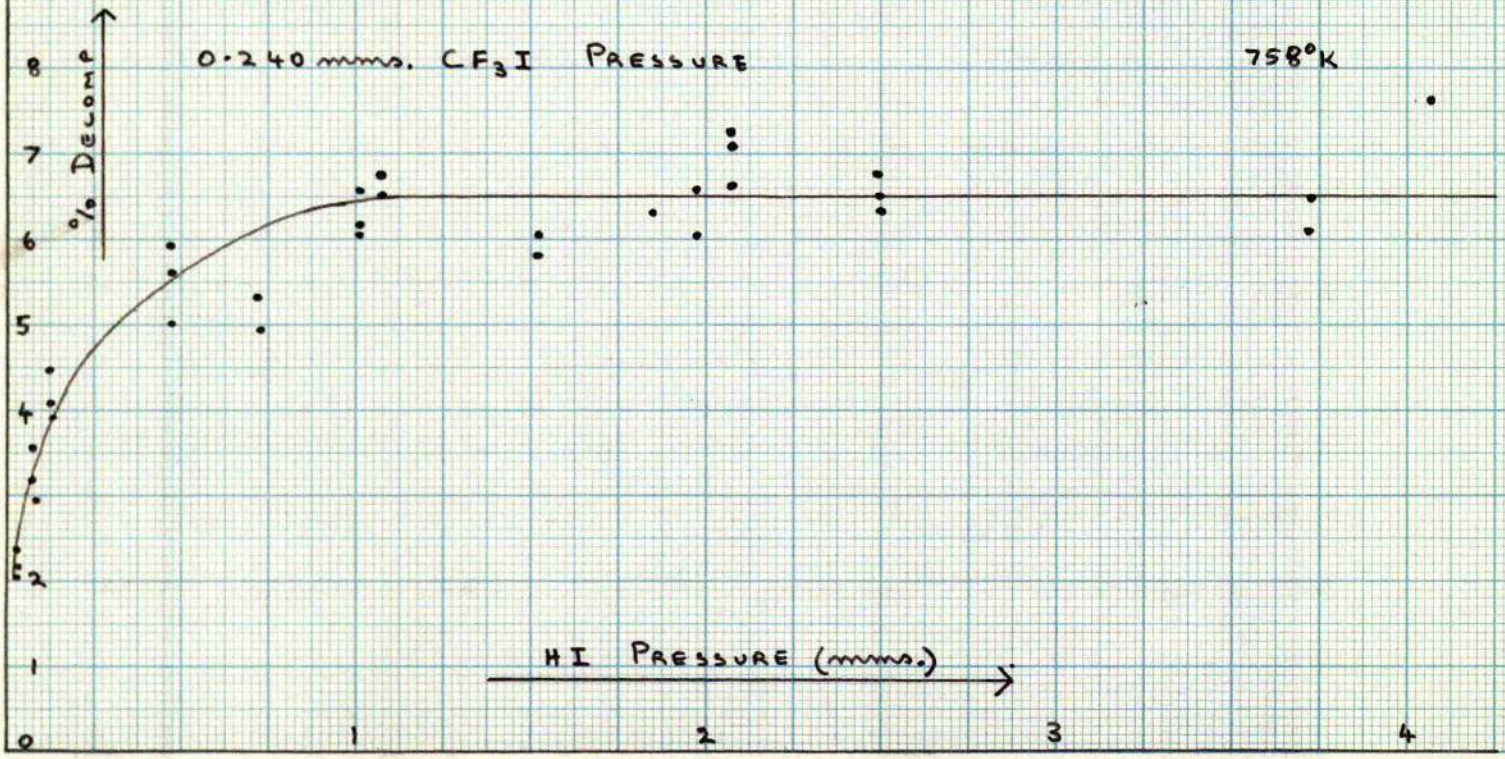


FIGURE 27b HI PRESSURE vs. PERCENTAGE DECOMPOSITION OF CF_3I CORRECTED TO 0·500 secs. CONTACT TIME AND 0·240 mms. CF_3I PRESSURE 758°K



scattered plot than in figure 27a. The reason for this correction is explained in the section on the variation of CF_3I pressure.

It is seen from figure 27a that the percentage decomposition at first increases with increase in HI pressure, but that above about 1 mm. of HI, it remains virtually constant: thus the bimolecular reaction

$$CF_3I + HI \longrightarrow CF_3H + I_2$$

cannot be one of the main sources of iodine under the experimental conditions. The horizontal portion of the graph in figure 27a can be interpreted as being due to the occurrence of the following reactions only:-

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

$$CF_3 + HI \longrightarrow CF_3H + I \qquad (15)$$

$$I + I \rightleftharpoons I_2 \qquad (3)$$

The variation of rate with HI pressure at low pressures of HI may be explained as being due to reaction (15) not removing all the CF_3 radicals, but some reacting by

$$CF_3 + I \longrightarrow CF_3I \qquad (2)$$

and $$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (4)$$

Reaction (5)

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (5)$$

must also take place, but very little C_2F_6 will be formed since the concentration of CF_3 radicals will be lower at this temperature; the main competition for CF_3 radicals is between iodine and HI. Under

the conditions where the rate is independent of HI pressure, the rate limiting step is reaction (1)

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

Variation of CF_3I Pressure.

Some evidence had been found in the work with toluene that the percentage decomposition depended on CF_3I pressure. Accordingly, a series of experiments were performed in which the CF_3I pressure was varied in the presence of sufficient HI to react with all the CF_3 radicals. The contact time was kept approximately constant in these experiments. The results are listed in table 14, and, corrected to 0.550 secs, are plotted in figure 28.

TABLE 14 Variation of CF_3I Pressure.

Temperature = 485°C = 758°K

Nitrogen carrier gas pressure varies 4.07 to 4.66 mms.

Expt. No.	CF_3I Pressure (mms)	HI Pressure (mms)	Contact Time (secs)	Percent Decomp.	Percent Decomp at .55 secs.
64a	.256	1.97	.559	6.7	6.6
b	.256	1.97	.559	7.3	7.2
65a	.254	2.50	.581	7.95	7.5
b	.254	2.50	.581	8.4	7.95
c	.254	2.50	.581	7.7	7.5
68a	.241	2.08	.526	7.5	7.85
b	.241	2.08	.526	7.7	8.05
c	.241	2.08	.526	7.0	7.3
74a	.479	2.12	.572	12.8	12.5
b	.479	2.12	.572	13.2	12.7
75a	.321	2.20	.570	9.55	9.0
b	.321	2.20	.570	10.0	9.6
c	.321	2.20	.570	9.2	8.9
76	.130	2.33	.545	5.1	5.15
77a	.581	2.14	.554	13.8	13.8
b	.581	2.14	.554	14.3	14.3
78a	.077	2.28	.553	3.70	3.7
b	.075	2.22	.539	3.44	3.5

FIGURE 28

PERCENTAGE DECOMPOSITION OF CF_3I IN 0.550 secs.

vs CF_3I PRESSURE

758°K

HI PRESSURE 1.97 to 2.33 mms.

N_2 CARRIER GAS PRESSURE 4.07 to 4.66 mms.

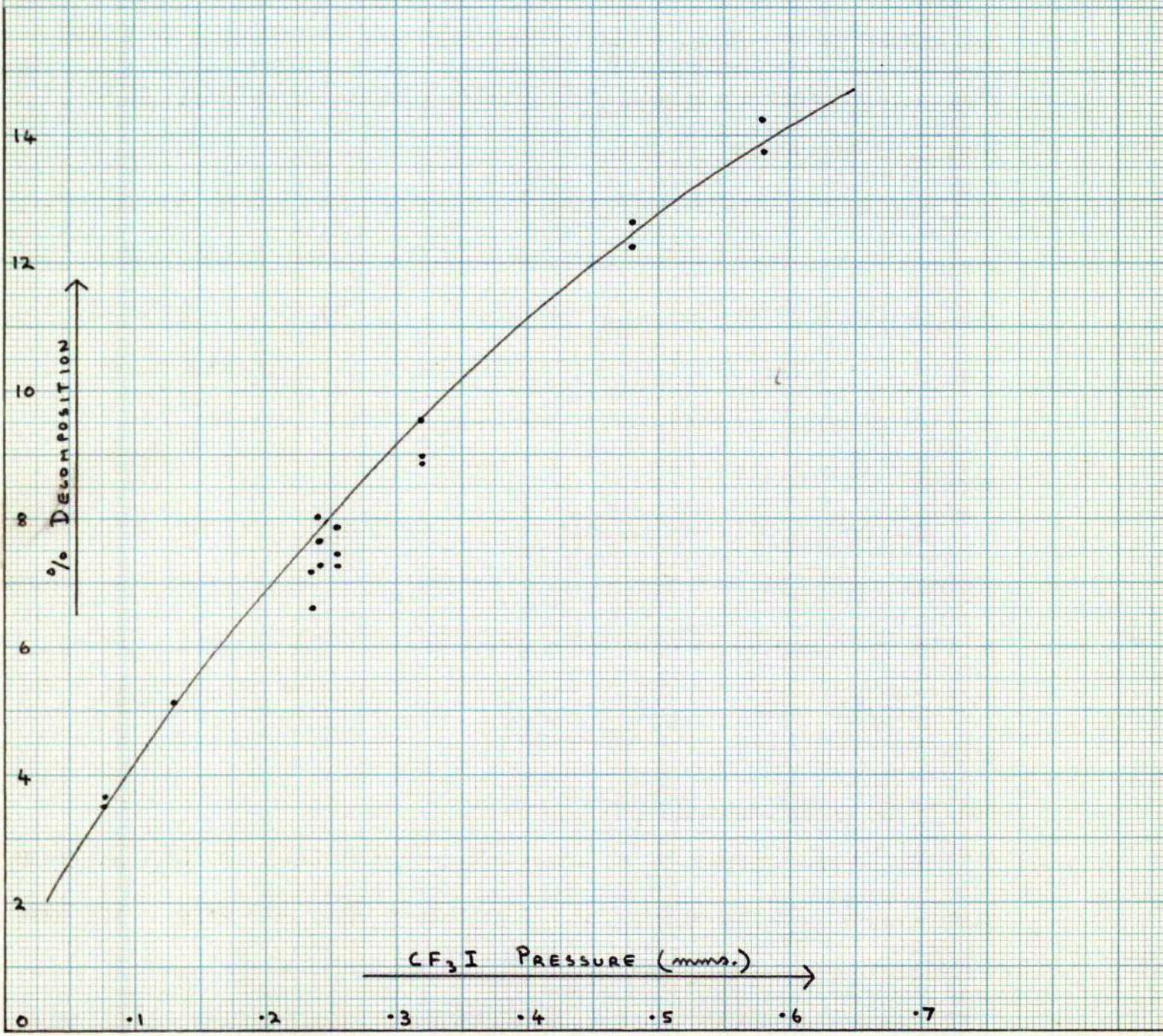


Figure 28 shows that the percentage decomposition is dependent upon CF_3I pressure, the rate being almost second order in CF_3I at the lowest concentrations. Assuming that the rate of iodine production is second order in CF_3I, the data on the variation of HI pressure which had already been corrected to .50 secs. contact time have also been corrected to .240 mms. pressure. The percentage decompositions of .24 mms. of CF_3I at .50 secs contact time at various HI pressures are listed in the final column of table 15 and are plotted in figure 27b. This graph is of the same general form as figure 27a but is much less scattered.

Collision theories of unimolecular reactions predict that at low pressures, all unimolecular reactions should become second order. It was thought that the second order behaviour in this reaction might be due to this cause, for this effect had been found with CH_3I under similar pressure conditions and had been explained according to this theory.

One method of checking this theory would be to vary the pressure of some inert gas at a fixed pressure of CF_3I. Increase in the pressure of the inert gas should raise the percentage decomposition. Series of experiments were therefore performed in which the carrier gas pressures were varied.

Variation of Nitrogen Pressure.

In these experiments an attempt was made to keep the CF_3I pressure constant at .100 mms and to make the contact time .550 secs. The data

have been corrected to these values for the purpose of plotting figure 29. The HI pressure was kept at approximately 1.0 mms.

TABLE 15 Variation of Nitrogen Pressure

Temperature = 485°C = 758°K.

Expt. No.	Pressure CF_3I (mms)	Pressure HI (mms)	Pressure N_2 (mms)	Contact Time (secs)	Percent Decomp	% Dec at .55secs and .10 mms. CF_3I
79a	.0985	1.015	2.57	.542	2.98	5.06
b	.0985	1.015	2.57	.542	3.22	5.32
80a	.099	1.01	8.15	.546	4.85	5.0
b	.099	1.01	8.15	.546	4.25	4.35
81a	.086	1.14	14.5	.540	4.8	5.7
b	.086	1.14	14.5	.540	4.3	5.15
82a	.102	1.10	5.15	.555	4.20	4.08
b	.102	1.10	5.15	.555	3.95	3.82
83a	.098	1.01	12.1	.548	4.95	5.05
b	.098	1.01	12.1	.548	4.75	4.85

Inspection of figure 29 shows that the percentage decomposition does increase slightly as the nitrogen pressure is raised.

Variation of Argon Pressure.

In order to see if a different effect could be produced by using another inert carrier gas, a similar series of experiments were performed with argon. The results, corrected as before, are also plotted on figure 29.

TABLE 16 Variation of Argon Pressure

Temperature = 485°C = 758°K

Expt. No.	Pressure CF_3I (mms)	Pressure HI (mms)	Pressure Argon (mms)	Contact Time (secs)	Percent Decomp.	% Dec at .55 secs and .10 mms CF_3I
84	.096	.985	12.4	.535	3.6	3.8
	.096	.985	12.4	.535	3.9	4.1
85	.105	1.07	2.65	.575	3.8	3.4
	.105	1.07	2.65	.575	3.8	3.4
86	.106	1.08	5.45	.597	4.25	3.65
	.106	1.08	5.45	.597	4.3	3.7
87	.098	1.01	8.25	.545	4.15	4.25
	.098	1.01	8.25	.545	3.95	4.1

It is seen that the effect of argon in increasing the rate is even smaller than the effect of nitrogen as would be expected.

Introduction of Benzotrifluoride.

Previous workers with this type of effect have found that, in general, the more complex a molecule is, the more efficient it is in transferring energy. Benzotrifluoride has previously been used as an activating gas in work with cyclopropane[101] and cyclobutane[102] and has been found to be much more efficient than nitrogen or argon. It was decided to use it here; the injection unit previously used for toluene was employed to introduce it into the gas stream. Trial experiments failed to detect any signs of its decomposition under

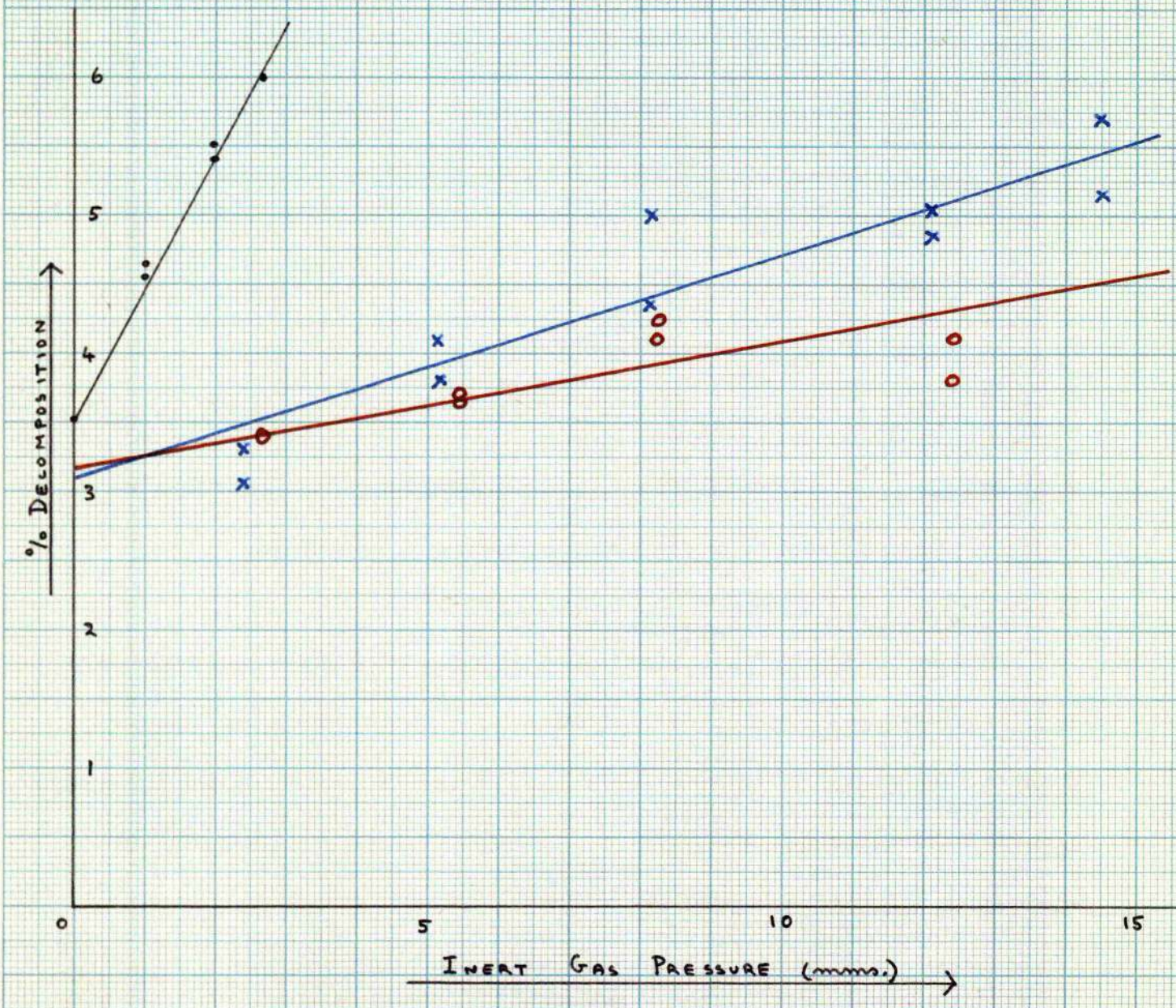
FIGURE 29

PERCENTAGE DECOMPOSITION OF 0·100 mms. CF_3I IN 0·550 secs. vs. INERT GAS PRESSURE. 758°K

= BENZOTRIFLUORIDE

= NITROGEN

= ARGON



experimental conditions and no reaction with HI was found. In the actual experiments with CF_3I, no unusual products were observed. Argon was used as carrier gas because its lower activating efficiency should make the effect of benzotrifluoride more noticeable.

TABLE 17 Variation of Benzotrifluoride Pressure.

Temperature = 485°C = 758°K

Expt. No.	CF_3I Pressure (mms)	HI Pressure (mms)	$PhCF_3$ Pressure (mms)	Argon Pressure (mms)	Contact Time (secs)	Percent Decomp	% Dec at .55 secs and .100 mms CF_3I
88a	.101	1.05	.99	5.42	.559	4.78	4.65
b	.101	1.05	.99	5.42	.559	4.68	4.55
89a	.0925	.980	1.99	5.58	.525	4.85	5.5
b	.0925	.980	1.99	5.58	.525	4.75	5.4
90a	.098	1.05	2.65	5.52	.545	5.85	6.0
b	.098	1.05	2.65	5.52	.545	5.8	5.95

From the data on the variation of argon pressure, the percentage decomposition of .100 mms CF_3I in 5.4 mms argon = 5.5%

These results are also plotted in figure 29

Figure 29 shows that the rate increases much more rapidly with rising benzotrifluoride pressure than it did with nitrogen pressure. From the sequence of activating efficiencies found, it would therefore appear that there is an inert gas effect of the type predicted by collision theories of unimolecular reactions.

The Efficiencies of the Inert Gases Used.

The relative efficiencies of these gases may be treated on a rather more quantitative basis. A quantity α_X may be defined as the efficiency of the gas X in transferring energy to CF_3I relative to the efficiency of $CF_3I = 1$. Values of α for the different inert gases used can be obtained from the experiments on the variation of inert gas pressure by using a method similar to that employed by Johnston[40] and given in detail in appendix (i).

In this method, the assumed first order rate constants for different inert gas concentrations at a fixed CF_3I concentration are plotted against the concentration of inert gas. The results for the experiments where the pressures of nitrogen, argon and benzotrifluoride were varied are presented in table 18 and in figure 30.

FIGURE 30

$k_{1st\ order}$ FOR DECOMPOSITION OF 0-100 mms. CF_3I vs. CONCENTRATION OF INERT GASES AT 758°K

—— = BENZOTRIFLUORIDE

—— = NITROGEN

—— = ARGON.

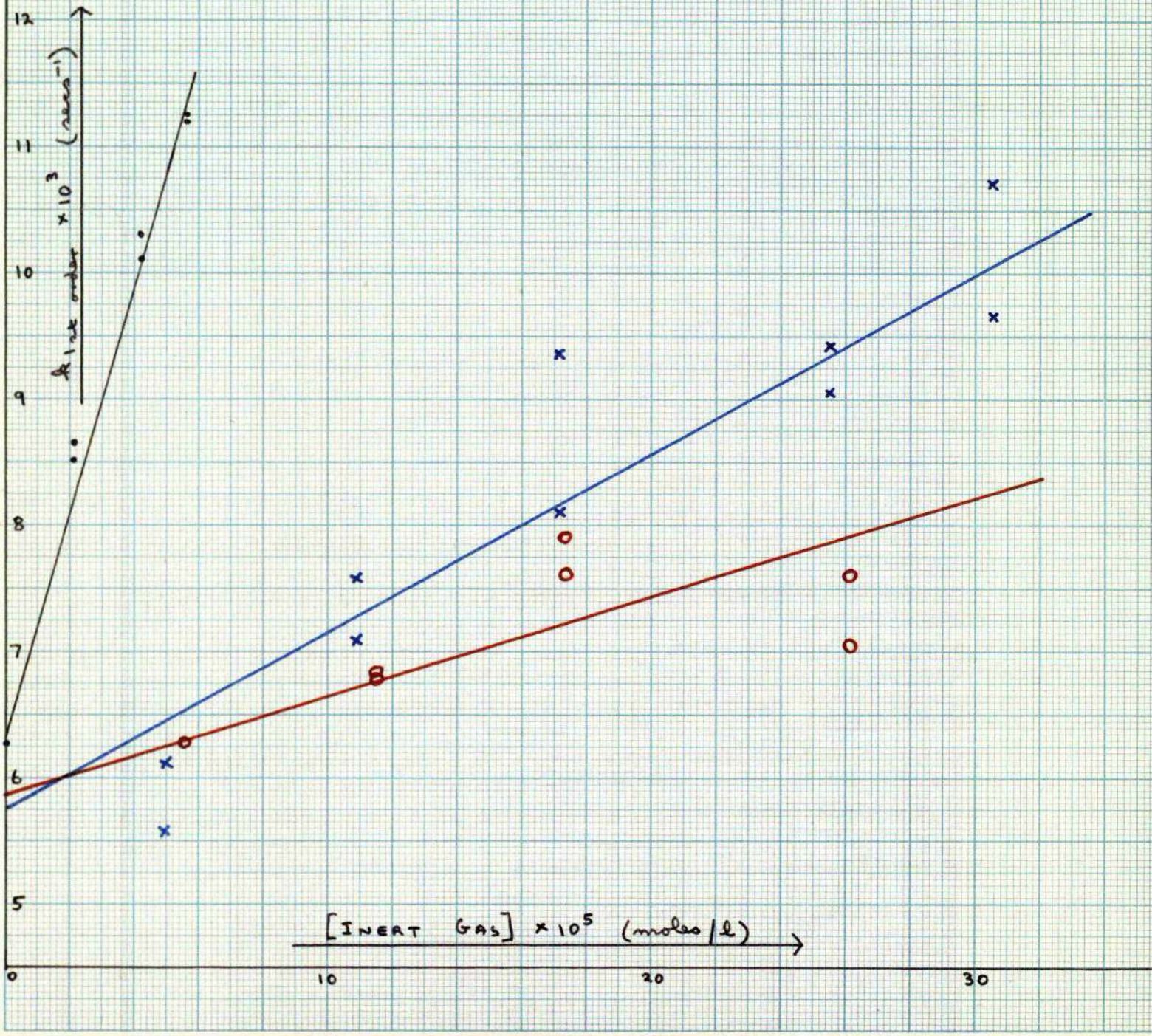


TABLE 18 Assumed First Order Rate Constants at Different Inert Gas Concentrations.

Nitrogen			Argon			Benzotrifluoride		
Expt No.	N_2 Concn. Moles/l x 10^5	k 1st order x 10^5 ($secs^{-1}$)	Expt No.	A Concn Moles/l x 10^5	k 1st order x 10^5 ($secs^{-1}$)	Expt No.	$PhCF_3$ concn. moles/l x 10^5	k 1st order x 10^5 ($secs^{-1}$)
79a	5.00	5.57	84a	26.2	7.04	88a	2.09	8.65
b	5.00	6.11	b	26.2	7.61	b	2.09	8.50
80a	17.2	9.55	85a	5.60	6.28	89a	4.21	10.3
b	17.2	8.08	b	5.60	6.28	b	4.21	10.1
81a	30.6	10.7	86a	11.5	6.77	90a	5.56	11.25
b	30.6	9.65	b	11.5	6.80	b	5.56	11.2
82a	10.9	7.57						
b	10.9	7.09	87a	17.4	7.90	-	0	6.26
83a	25.6	9.41	b	17.4	7.61			
b	25.6	9.05						

In each case, the plot in figure 30 is approximately a straight line. Provided that the reaction remains nearly second order in CF_3I, straight lines should be obtained, and in the cases of N_2 and A, the intercepts on the rate axis should be the same and should be the rate for the decomposition of .100 mms. CF_3I alone when the back reaction is prevented. The few mms. of argon present in the experiments with benzotrifluoride do not cause much increase in the rate of

decomposition of CF_3I and may be neglected for the purpose of evaluation of $\alpha_{C_6H_5CF_3}$.

The efficiency α of an inert gas is found from figure 50 by

$$\alpha = \frac{\text{(slope of line) (concentration } CF_3I)}{\text{(intercept on rate axis)}}$$

For N_2, $\alpha_{N_2} = .0052$

For A, $\alpha_A = .0029$

For $C_6H_5CF_3$, $\alpha_{C_6H_5CF_3} = .030$

According to the simple Lindemann theory of first order reactions, for a system containing only the reactant, a graph of $\frac{1}{k \text{ 1st order}}$ against $\frac{1}{\text{pressure of reactant}}$ should give a straight line. In the system under consideration, other gases were present as well as the reactant, CF_3I, and $\frac{1}{k \text{ 1st order}}$ should be plotted against $\frac{1}{\text{effective pressure}}$ where the effective pressure

$= P_{CF_3I} + \alpha_x P_x + \alpha_y P_y + \text{- - - - - - - - -}$

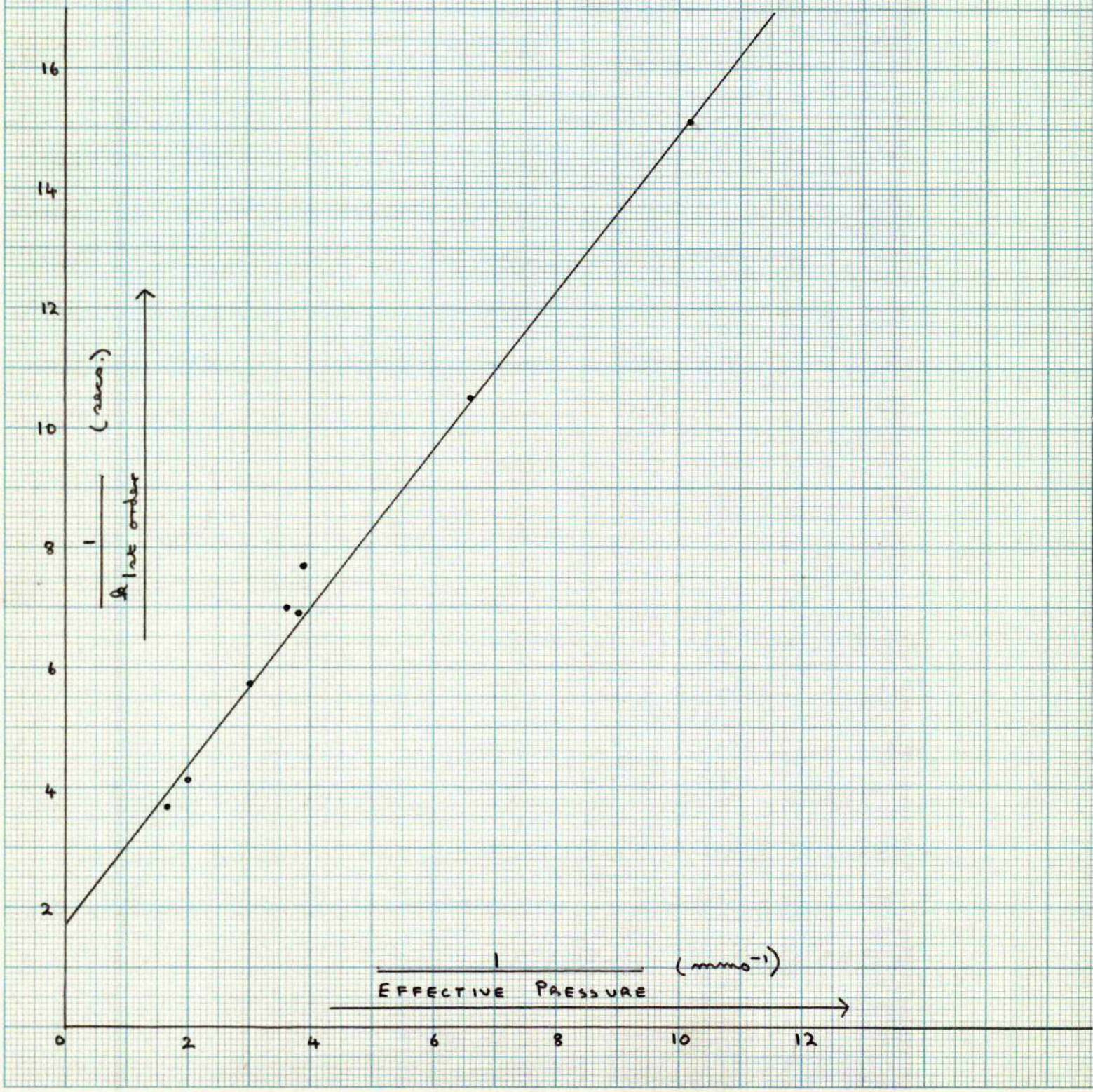
where x,y, - - - - are the other gases. (Appendix (i)).

For the system used here, the other gases are N_2 and HI, the products being ignored because of their very small concentration. Within the limits of experimental error, the pressure of HI appeared to have no effect on the rate of reaction over the range of concentration studied. Since only about 1 mm. of HI was present in any case, $\alpha_{HI} P_{HI}$ will be very small and may be neglected. Using the value $\alpha_{N_2} = .0052$, it is possible to calculate the effective pressure for the experiments

FIGURE 31

$\frac{1}{k_{1st\ order}} \sim \frac{1}{\text{EFFECTIVE PRESSURE}}$

758° K



where the pressure of CF_3I was varied. Table 19 contains this data, average values for the experiments being quoted.

TABLE 19 Effective Pressure and Assumed First Order Rate Constant

Expt No.	.0052 x N_2 Pressure (mms)	Pressure CF_3I (mms)	Effective Pressure (mms)	$\frac{1}{\text{(Effective Pressure)}}$ (mms.^{-1})	$\frac{1}{k_{1st\ order}}$ (secs)	$k_{1st\ order}$ (secs^{-1})
64	.0242	.236	.260	3.85	7.70	.130
65	.0239	.254	.278	3.60	7.00	.143
68	.022	.241	.263	3.80	6.90	.145
74	.022	.479	.501	2.00	4.13	.242
75	.0218	.321	.342	3.02	5.75	.174
76	.022	.150	.152	6.60	10.5	.095
77	.021	.581	.602	1.66	3.68	.272
78	.022	.076	.098	10.2	15.1	.0665

In figure 31 is plotted $\frac{1}{k\ 1st\ order}$ against $\frac{1}{(\text{Effective pressure})}$ and it is seen that a reasonable straight line is obtained. This would imply that the reaction does approximate to Lindemann type behaviour.

However, the absolute values of α range from .0029 to .030. In a review of reactions which undoubtedly show transitions from first to second order behaviour[9], the lowest quoted value of α for N_2 = .07, for argon is .07 and for benzotrifluoride is 0.75. The values

FIGURE 32

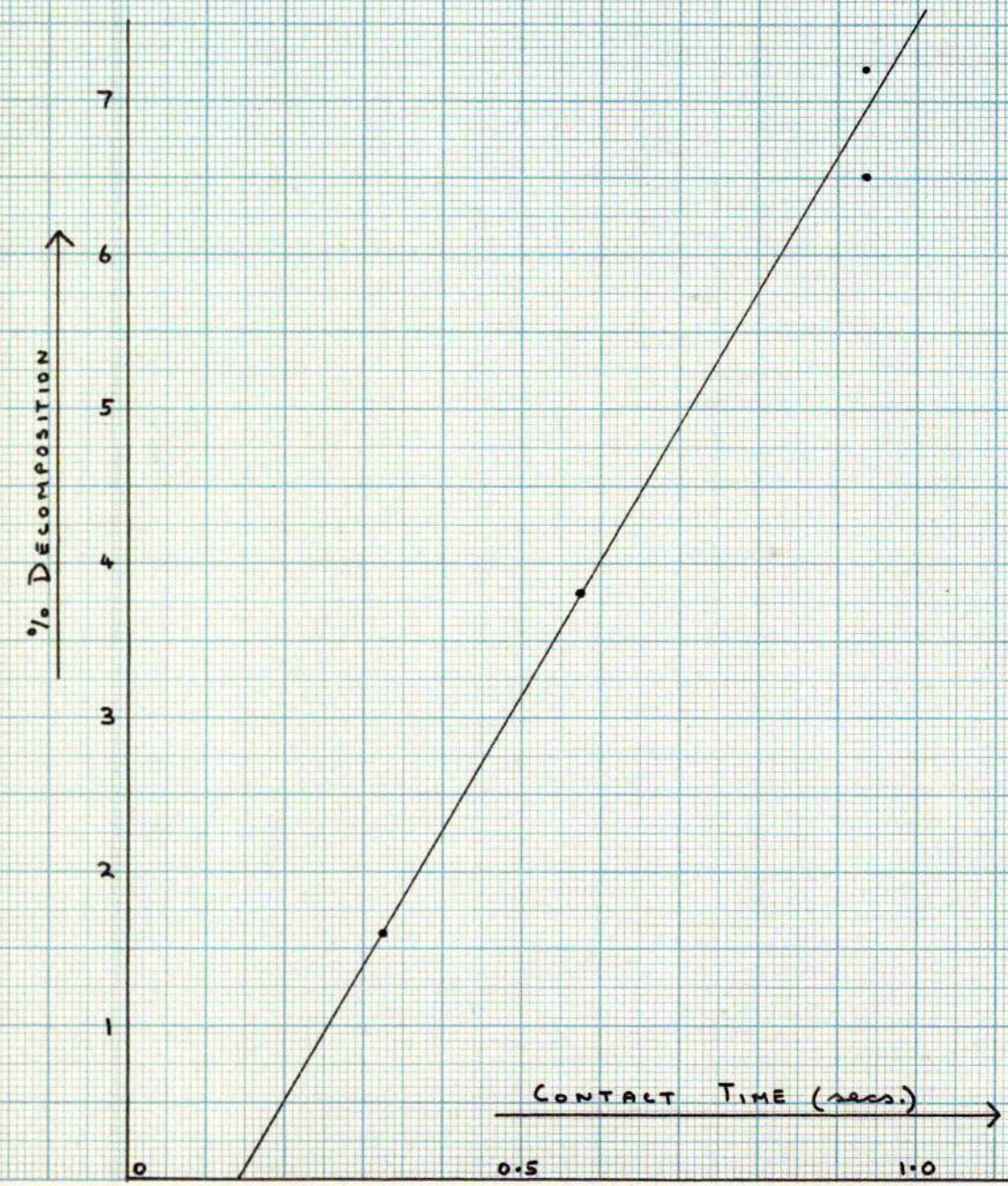
PERCENTAGE DECOMPOSITION OF 0·100 mmo. CF_3I

vs. CONTACT TIME

758°K

HI PRESSURE ·835 to 1·07 mmo.

ARGON CARRIER GAS PRESSURE 2·54 to 2·86 mmo.



obtained here are a factor of 10 to 20 lower than these literature values which make it seem unlikely that the change in rate as the CF_3I pressure is altered is wholly due to the effect suspected.

Variation of Contact Time.

In all the work so far done in the pyrex vessel, it had been attempted to perform series of experiments at constant contact times; the usual variation from the desired time was less than $\pm$ 5%. No systematic variation of contact time had been performed, however, and it was decided to do this. A pressure of CF_3I of 0.1 mms. was chosen and argon was used as carrier gas. The results are given in table 20, and, corrected to .100 mms., are plotted in figure 32.

TABLE 20 Variation of Contact Time

Temperature = 758° K. Argon Pressure = 2.54 to 2.86 mms.

Expt. No.	Pressure CF_3I (mms)	Pressure HI (mms)	Contact Time (secs)	Percent Decomp	Percent Dec. at .10 mms. CF_3I
85a	.105	1.07	.575	5.80	5.62
b	.105	1.07	.575	5.80	5.62
91a	.101	.835	.526	1.61	1.60
b	.101	.835	.526	1.60	1.58
92a	.095	1.03	.934	6.20	6.50
b	.095	1.03	.934	6.90	7.20

Figure 32 shows that if a straight line is drawn through the experimental points then this line does not pass through the origin

of the graph. A similar effect has been found by Lapage[105] and was thought to be due to some characteristic of the flow system - perhaps the need for a warming up period for the gases. It was assumed that the same effect was causing this phenomenon. No serious error should result from correction over small contact time variations; it was therefore decided to use the nominal contact time in calculations but to attempt to keep the contact time as constant as possible. This approximation should make all the nominal rate constants wrong by the same factor.

After these experiments, the pyrex glass reactor was removed. There was a slight "blackening" over approximately what had been regarded as the "hot length". It was assumed that this blackening was due to a carbon deposit but it was not strictly proved to be carbon for the rate of oxidation is very slow at the temperatures to which pyrex may be heated. This carbon deposit actually in the reaction zone indicates that it was formed on the walls. If it had been produced in the gas phase, it would probably have been carried along at least part way towards the exit of the reactor. The most probable explanation is that some of the CF_3 radicals which could not be accounted for when using toluene decomposed on the walls to give carbon. The fluorine which must also have been produced would react with the glass to form SiF_4 but was undetected, probably because of the impurity already present. No attempt was made to estimate the carbon, for its rate of oxidation at the temperatures to which pyrex

can be heated is very slow. The amount formed in one experiment must have been very small for the cumulative effect produced a transparent coating.

Variation of Surface Area and of Temperature.

No work had yet been done to test whether the reaction was homogeneous or not. Accordingly, a reaction vessel was constructed in which the thermocouple well and exit tube were detachable. Two liners could be inserted and these affected the dimensions as follows:-

	Surface Area	Volume	$\frac{S}{V}$ (cms^{-1})
No liners	574 cms^2	295 mls.	1.95
1 liner	1,018 cms^2	257 mls.	3.96
2 liners	1,598 cms^2	228 mls.	6.15

Thus an alteration of a factor of three in $\frac{S}{V}$ was possible. The experiments were performed with a CF_3I pressure close to .10 mms., with a low pressure of argon and at a contact time near .750 secs. The initial work was carried out at 758°K, the temperature at which the previous work with HI was performed.

TABLE 21 Effect of Surface Area at 758°K

Argon Pressure = 5.41 to 5.60 mms.

Expt. No.	$\frac{S}{V}$ cms^{-1}	Pressure CF_3I (mms)	Pressure HI (mms)	Contact Time (secs)	Percent Decomp	% Dec at .10 mms CF_3I and .75 secs C.T.
95a	1.95	.099	.995	.755	3.61	3.65
b	1.95	.099	.995	.755	3.57	3.61
94a	3.96	.107	1.01	.775	6.95	6.30
b	3.96	.107	1.01	.775	6.90	6.25
95a	6.15	.0955	1.04	.722	7.55	8.0
b	6.15	.0955	1.04	.722	7.20	7.85

It is seen that the rate increases as the surface area is enlarged. In order to see if the activation energy of the reaction was affected by the surface, three series of experiments were performed in which the temperature was varied at each surface to volume ratio. If the reaction proceeds either completely in the gas phase or completely on the surface, the activation energy should remain independent of S/V. If, however, there is an increasing amount of surface reaction at higher $\frac{S}{V}$ ratio, a change in activation energy would be expected since it is unlikely that a homogeneous and a surface reaction will have identical activation energies.

The experiments were performed at a CF_3I pressure of .10 mms. where the reaction is second order in CF_3I. If it was correct that

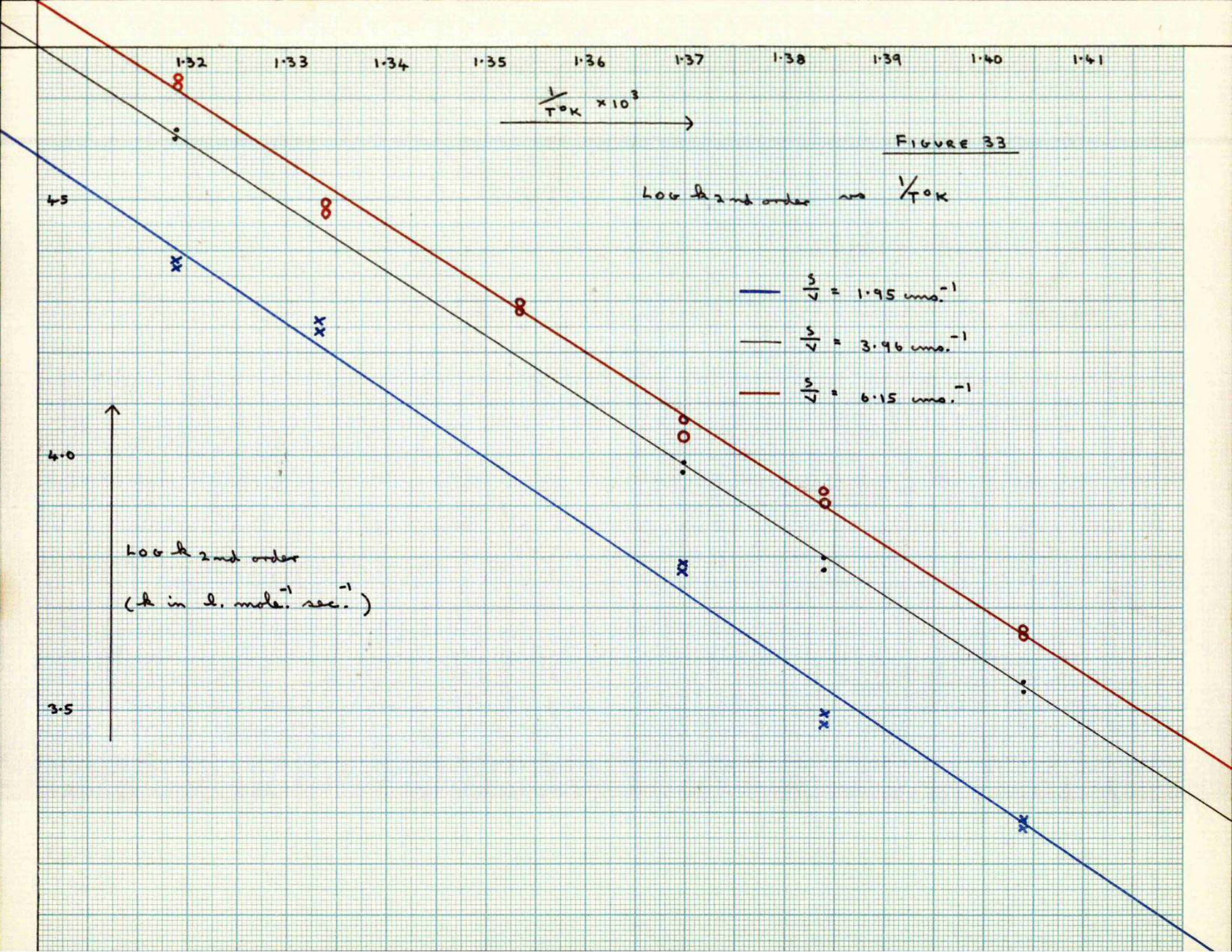

1·32
1·33
1·34
1·35
1·36
1·37
1·38
1·39
1·40
1·41
1/T°K × 10³
4·5
4·0
3·5
Log k 2nd order
(k in l. mole⁻¹ sec⁻¹)
Log k 2nd order vs 1/T°K
— S/√ = 1·95 mm.⁻¹
— S/√ = 3·96 mm.⁻¹
— S/√ = 6·15 mm.⁻¹

FIGURE 33

the change in rate of reaction with alteration in pressure of CF_3I was due to activation according to the Lindemann theory, then a plot of log $k_{\text{second order}}$ against $\frac{1}{T}{}^{o}K$ should yield the activation energy required to make CF_3I molecules sufficiently active to decompose. $k_{\text{second order}}$ is the assumed second order rate constant for the decomposition of CF_3I and is evaluated from the expression

$$k_{\text{second order}} = \frac{1}{t} \frac{x}{a(a-x)} \qquad (1 \text{ mole}^{-1} \text{ sec}^{-1})$$

where t = contact time (secs)

x = moles/l iodine at exit to reactor

a = initial concentration of CF_3I in moles/l.

If the interpretation of the kinetics is correct and if the reaction

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

is the rate limiting step, then the activation energy should be identifiable with $D(CF_3 - I)$.

The results are listed in tables 22, 23 and 24 and figure 33 is a graph from which activation energies may be calculated.

TABLE 22 Variation of Temperature at $\frac{S}{V}$ = 1.95 cms^{-1}

Argon Pressure = 3.51 to 3.60 mms. HI Pressure = 0.98 to 1.01 mms.

Expt. No.	Pressure CF_3I (mms)	Contact Time (secs)	Percent Decomp	$k_{2nd\ order}$	log $k_{2nd\ order}$	T (°K)	$\frac{1}{T} \times 10^3$
95a	.099	.755	3.61	2.38×10^4	4.377	758	1.319
b	.099	.755	3.57	2.35×10^4	4.371	758	1.319
97a	.098	.774	1.005	6.10×10^3	3.785	730	1.370
b	.098	.774	.99	6.01×10^3	3.779	730	1.370
102a	.1025	.808	.550	2.91×10^3	3.463	722.5	1.384
b	.1025	.808	.568	3.09×10^3	3.490	722.5	1.384
101a	.1005	.814	.348	1.90×10^3	3.278	712	1.404
b	.1005	.814	.338	1.85×10^3	3.267	712	1.404
107a	.099	.769	2.91	1.84×10^4	4.265	749.5	1.334
b	.099	.769	2.76	1.74×10^4	4.241	749.5	1.334

TABLE 23 Variation of Temperature with $\frac{S}{V}$ = 3.96 cms^{-1}

Argon Pressure = 3.42 to 3.51 mms. HI Pressure = .91 to 1.02 mms.

Expt. No.	Pressure CF_3I (mms)	Contact Time (secs)	Percent Decomp	$k_{2nd\ order}$	log $k_{2nd\ order}$	T (°K)	$\frac{1}{T} \times 10^3$
94a	.107	.775	6.95	4.24×10^4	4.627	758	1.319
b	.107	.775	6.90	4.21×10^4	4.624	758	1.319
98a	.098	.788	1.60	9.60×10^3	3.982	730	1.370
b	.098	.788	1.535	9.20×10^3	3.964	730	1.370
99a	.102	.815	1.165	6.33×10^3	3.801	722.5	1.384
b	.102	.815	1.08	5.9×10^3	3.771	722.5	1.384

Table 25 Con.

Expt. No.	Pressure CF_3I (mms)	Contact Time (secs)	Percent Decomp	$k_{2nd\ order}$	log $k_{2nd\ order}$	T (^oK)	$\frac{1}{T} \times 10^3$
100a	.101	.805	.64	3.53×10^3	3.548	712	1.404
b	.101	.805	.618	3.42×10^3	3.534	712	1.404

TABLE 24 Variation of Temperature with $\frac{S}{V}$ = 6.15

Argon Pressure = 3.41 to 3.56 mms. HI Pressure = .91 to 1.04 mms.

Expt. No.	Pressure CF_3I (mms)	Contact Time (secs)	Percent Decomp	$k_{2nd\ order}$	log $k_{2nd\ order}$	T (^oK)	$\frac{1}{T} \times 10^3$
95a	.0955	.722	7.35	5.46×10^4	4.737	758	1.319
b	.0955	.722	7.20	5.35×10^4	4.728	758	1.319
96a	.098	.754	1.82	1.142×10^4	4.061	730	1.370
b	.098	.754	1.72	1.08×10^4	4.033	730	1.370
103a	.103	.775	1.46	8.37×10^3	3.923	722.5	1.384
b	.103	.775	1.40	8.00×10^3	3.903	722.5	1.384
104a	.1015	.799	.82	4.53×10^3	3.656	712	1.404
b	.1015	.799	.79	4.37×10^3	3.641	712	1.404
105a	.1035	.776	3.30	1.96×10^4	4.293	739	1.353
b	.1035	.776	3.24	1.93×10^4	4.285	739	1.353
106a	.1015	.742	4.70	3.07×10^4	4.487	749.5	1.334
b	.1015	.742	4.51	2.95×10^4	4.470	749.5	1.334

The activation energies E and the temperature independent factors B in the Arrhenius equation $k = Be^{-E/RT}$

for the different lines are

S/V (cms^{-1})	E (k cals/mole)	$\log_{10}B$ (k in l $mole^{-1}$ sec^{-1})
1.95	59.8	21.6
3.96	57.5	21.2
6.15	57.5	21.5

Within the limits of experimental error, the activation energies for the three lines are the same. Thus it would appear that the reaction proceeds by the same mechanism independent of S/V. The fact that the rate is affected by S/V would appear to indicate a reaction on the surface. However, the activation energy is of the correct order of magnitude for $D(CF_3\text{-}I)$, and if the whole reaction was catalytic on the surface, it would be expected that the activation energy would be less than $D(CF_3\text{-}I)$.

The temperature independent factors of about 10^{21} are much greater than the normal bimolecular collision frequency of about 10^{11} $l.mol^{-1}$ sec^{-1}. With this type of reaction, however, a value of log B = 11 would not be expected.

If a value of 58.5 k cals/mole is correct for $D(CF_3\text{-}I)$ and if we estimate the first order rate constant by

$$k = 10^{13} \exp\left(\frac{-58{,}500}{RT}\right) secs^{-1}$$

we have at 758°K $k_{1st\ order} = 1.5 \times 10^{-4} secs^{-1}$. This is about a thousand fold less than the experimental "first order rate constants" of table 19. It would therefore appear that if the reaction is showing a transition from second to first order, then it will have an unusually

high pre-exponential factor under first order conditions. This might suggest that the reaction is in fact more complicated than we have hitherto supposed.

After these experiments, the reactor was examined for carbon deposit. None was found; this confirms the view that the production of carbon occurred during the experiments where toluene was added and failed to react with all the radicals.

Addition of Iodine.

These experiments were in fact the last to be performed. They were carried out because it had been found that the reaction was iodine catalysed under the conditions used in the sealed bulbs and it was suspected that the same type of behaviour might occur in the flow system. The results have been included here in order to present all the flow system data together.

The work was carried out in the reaction vessel with the detachable end without any liners inside. A partial pressure of CF_3I of .10 mms. was used since so much of the work had been done with this pressure. Argon was again used as carrier gas and an attempt was made to keep the contact time constant at .750 secs. The results are given in table 25 and are plotted in figure 54.

TABLE 25 Addition of Iodine to Flow System

Temperature = 758°K. Argon Pressure = 5.57 to 5.69 mms.
Contact Time = .749 to .758 secs.

Expt. No.	Pressure CF_5I (mms)	Pressure HI (mms)	Pressure I added (mms)	% Dec. at .100 mms. CF_5I
108a	.102	.985	0	5.05%
b	.102	.985	.00895	10.8%
109a	.100	1.01	0	5.63%
b	.100	1.01	.0176	13.0%
110a	.101	.99	0	4.1%
b	.101	.99	.00586	8.85%
111a	.104	2.17	0	5.5%
b	.104	2.17	.0155	12.9%
Temperature = 698°K Argon Pressure = 5.89 mms. Contact Time = .855 secs.				
112a	.105	2.02	.0090	.77%
b	.105	2.02	.0090	.685%

The "Pressure I added" is calculated assuming that the iodine added is completely dissociated into atoms. In most cases, the iodine is more than 50% dissociated into atoms, so this is a reasonable approximation for the rather qualitative purposes of figure 34. The hot volume of the reaction vessel in the above experiments was

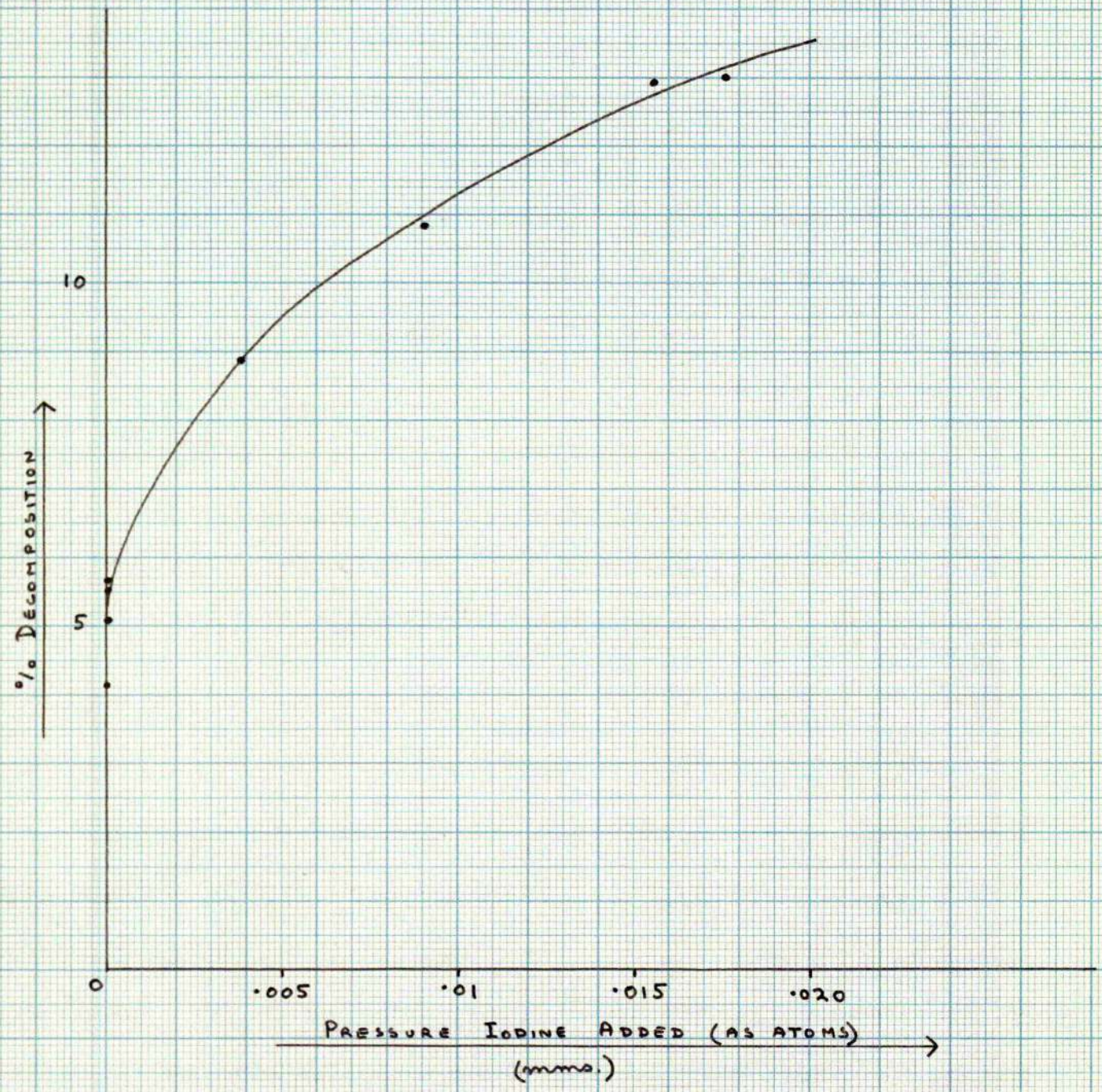
FIGURE 34

EFFECT OF ADDITION OF IODINE ON

PERCENTAGE DECOMPOSITION

TEMPERATURE = 758°K CONTACT TIME = ·750 msec.

CF_3I PRESSURE = ·100 mms.



nominally the same as when the temperature variation experiments were performed. Nevertheless, the rate constant when no iodine was added is about 50% higher than was obtained previously; this is probably due to errors in the measurement of the reaction volume and the experimental values obtained above were employed in making calculations.

Figure 54 shows qualitatively that the rate of production of iodine increases as more iodine is added. In experiment 112, very little decomposition would have occurred under these conditions if no iodine had been added initially.

It is possible that this increase in percentage decomposition is due to the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

The reverse reaction

$$CF_3 + I_2 \longrightarrow CF_3I + I$$

is prevented by the reaction of CF_3 radicals with HI.

The experimental data can be treated in such a manner as to show that it obeys approximately the kinetic law:-

$$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2(CF_3I)(I)$$

and to obtain a value for C_2.

C_1 and C_2 are constants related to the specific rate constants.

A graph of $\frac{d(I_2)}{dt}$ against (I) at constant CF_3I concentration should be a straight line with slope = $C_2(CF_3I)$ and making an intercept on the (I)=0 axis of $C_1(CF_3I)$. Actual values of $\frac{d(I_2)}{dt}$ and(I) at any instant cannot be obtained from the available data, and it would

be technically difficult to produce them with the apparatus used, but it is possible to calculate approximately mean values of $\frac{d(I_2)}{dt}$ and of (I) from experiments 108 to 112.

The mean rate of formation of iodine may be calculated directly. The values of $\frac{d(I_2)}{dt}$ for experiments 108 to 111 have been corrected to .100 mms. CF_3I for the purpose of plotting figure 35. The mean iodine atom concentration can be found approximately in the following manner. The concentration of iodine atoms at the beginning of the reaction may be found from a knowledge of the total iodine present and the fraction dissociated (Appendix (ii)). The concentration of iodine atoms at the end of the reaction may similarly be evaluated. The arithmetic mean of these two values gives a reasonable value of the effective average iodine atom concentration for use in the rate law expression.

Table 26 contains these quantities evaluated for experiments 108 to 112 and figure 35 is a graph of the data at 758°K.

FIGURE 35

MEAN RATE OF FORMATION OF IODINE vs.

MEAN IODINE ATOM CONCENTRATION

758°K

CF_3I PRESSURE = 0·100 mms.

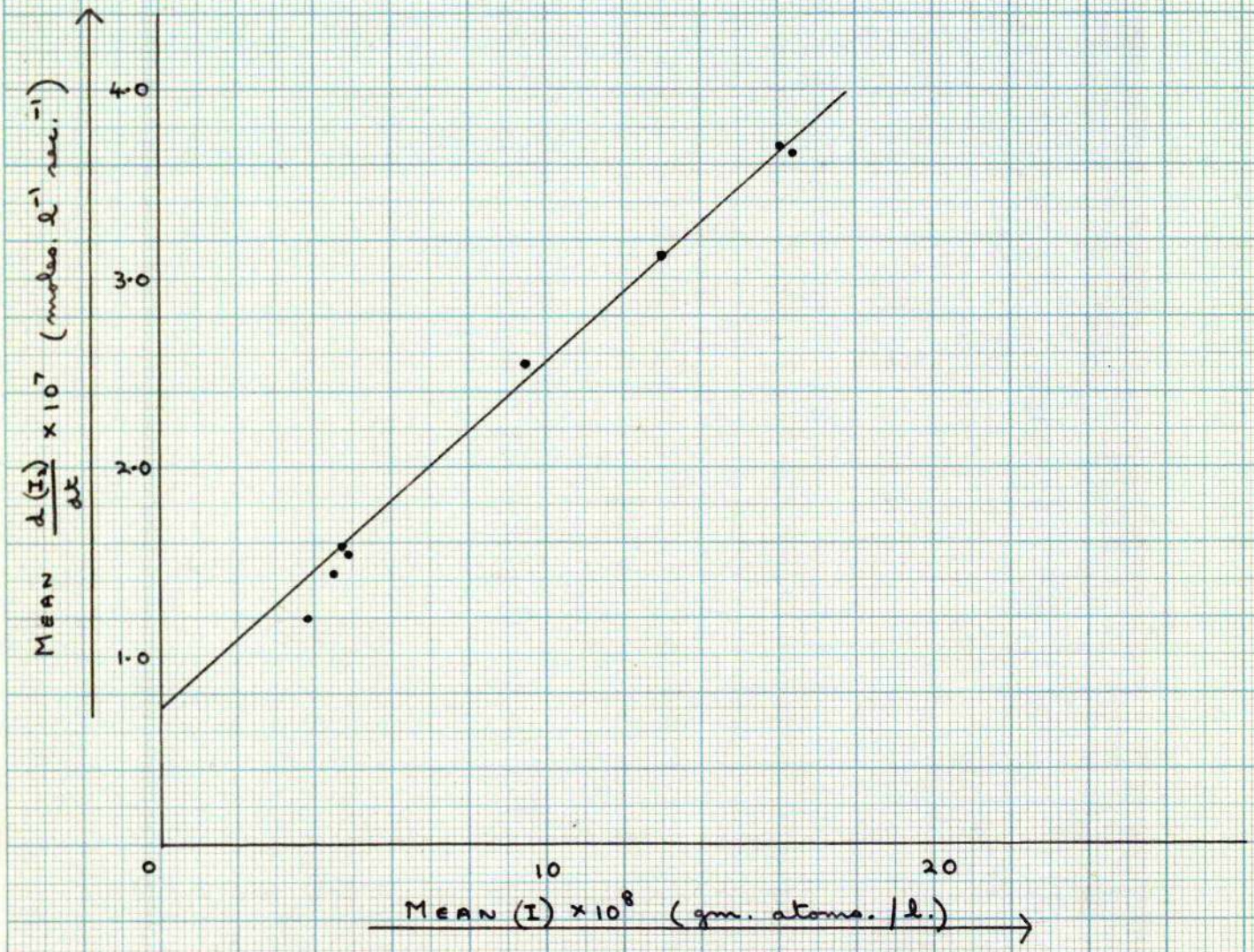


TABLE 26 Effect of I atom concentration on $\frac{d(I_2)}{dt}$

Expt. No.	Tempr (°K)	CF_3I Pressure (mms)	$(I)\times10^8$ Initial	$(I)\times10^8$ Final	Mean $(I)\times10^8$	Mean $\frac{d(I_2)}{dt} \times 10^7$ at .10 mms CF_3I
108a	758	.102	0	9.00	4.50	1.455
b	758	.102	8.15	17.7	12.95	3.12
109a	758	.100	0	9.40	4.70	1.59
b	758	.100	12.5	20.5	16.40	5.65
110a	758	.101	0	7.74	3.87	1.18
b	758	.101	4.74	14.15	9.45	2.54
111a	758	.104	0	9.70	4.85	1.58
b	758	.104	11.45	20.65	16.05	5.68
112a	698	.105	3.68	4.00	3.84	.218
b	698	.105	3.68	3.96	3.82	.193

The iodine atom concentrations are in units of gm. atoms/l

$\frac{d(I_2)}{dt}$ is in units of moles l^{-1} sec^{-1}

Figure 55 shows that there is a straight line relationship between $\frac{d(I_2)}{dt}$ and the mean (I). From the intercept,

$C_1(CF_3I) = .72\times10^{-7}$ moles l^{-1} sec^{-1} at 758°K for a pressure of CF_3I of .10 mms.

From the slope $C_2 = 8.65\times10^5$ l. sec^{-1} gm. $atoms^{-1}$

At 698°K, the rate of production of iodine due to the term $C_1(CF_3I)$ may be ignored and this yields a mean value for C_2 at 698°K of

2.33×10^{5} l.sec^{-1} gm. $atoms^{-1}$.

The quantitative effect of these results upon the other data from the flow system and their relation to the findings in the sealed tube experiments are treated in the discussion section.

The Static Reactions in Sealed Tubes.

At the time this work was undertaken, the experiments in which iodine was added to the flow system had not been performed and it was not realised that the reaction was iodine catalysed. It was thought that at a sufficiently high pressure, the rate of decomposition should be first order in CF_3I. High pressures of CF_3I and the much higher pressures of HI which would be required to stop back reaction would be difficult to achieve in a flow system, and since sufficient material for analysis can be obtained in a fairly small volume at high pressures, there was little need for the flow technique. It was therefore decided to use a static system. The simplest type of system is probably that adopted here where sealed vessels are inserted into a furnace. This has the disadvantage that the exact time of start of the reaction is not known, but, if the temperature is chosen so that the warming up period is a small fraction of the reaction time, this is not important. A more elaborate system where the reaction vessel was kept permanently inside a furnace and the reactants introduced through a valve system would have been more difficult to construct and would not have yielded results of much higher accuracy.

Variation of HI Pressure and Decomposition of HI.

The first set of experiments were conducted to find if it would be possible to attain conditions where the rate of decomposition of CF_3I was independent of HI pressure when the other reaction variables remained constant. At the temperature at which this work was done,

there should, according to the data of Bodenstein, have been no detectable decomposition of HI. Nevertheless, small amounts of iodine were formed when HI was heated alone at the reaction temperatures. The amount of iodine formed appeared to be independent of the pressure of HI and may have been due to a zero order surface reaction. This decomposition of HI was not examined further. Taylor[104] has also found that the decomposition of HI is catalyzed by glass and silica. In experiments using CF_3I, an attempt was made to produce sufficient iodine so that the decomposition of the HI would be negligible in comparison. This resulted in a fairly high percentage decomposition of the CF_3I. The results are listed in table 27 and are plotted in figure 36.

The prefix S has been used to denote experiments performed in sealed bulbs.

FIGURE 36 STATIC EXPERIMENTS

EQUIVALENTS I_2 FORMED vs. MOLES HI PRESENT

• • = HI WITH 1·70 @ 1·73 × 10^{-4} MOLES CF_3I

• • = HI ALONE

522°K

REACTION TIME = 10,800 secs.

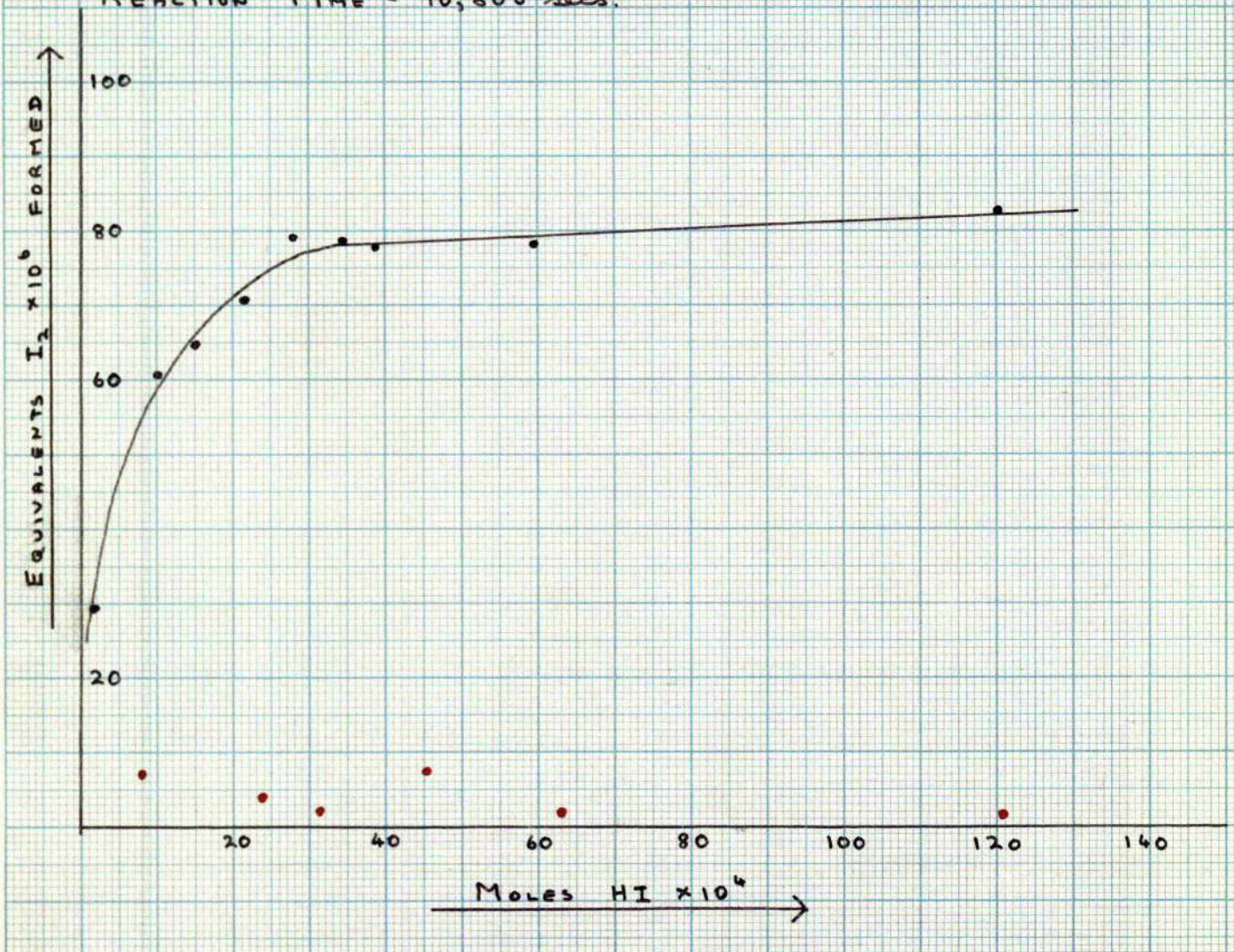


TABLE 27 Variation of HI pressure.

Temperature = 249°C = 522°K. Reaction Time = 3 hrs.= 10,800 secs.

Expt. No.	Moles $CF_3I \times 10^4$	Pressure CF_3I (mms)	Moles HI $\times 10^4$	Pressure HI (mms)	Equivs I_2 Produced $\times 10^6$
S1	-	-	7.75	36	6.9
S2	-	-	23.5	109	4.0
S3	1.72	8.00	14.8	69	64.5
S4	-	-	31.2	145	2.1
S5	-	-	45	210	7.2
S6	1.75	8.05	21.5	100	70.7
S7	1.75	8.05	28.0	130	79
S8	1.71	7.95	34.3	160	78.5
S9	1.72	8.00	38.5	175	77.7
S10	1.71	7.95	1.25	5.7	29.0
S11	1.71	7.95	10.2	47.5	60.5
S12	-	-	62.4	290	1.8
S13	1.70	7.90	59.3	229	78
S14	-	-	121	565	1.8
S15	1.71	7.95	120	560	82.5

These experiments were performed with up to 24% decomposition of the CF_3I. Inspection of figure 56 shows that at first, the amount of iodine produced increases with increasing HI pressure but that it then becomes almost independent of HI pressure. Because of the

scatter of the results and the trouble with the HI blank decomposition, it is impossible to tell from the experimental data if the rate is, in fact, completely independent of HI pressure. The experiments do show, however, that the rate is not strongly dependent on HI pressure. If the results are interpreted in the same way as the flow system data, this means that HI must be efficient in reacting with almost all the CF_3 radicals and that the bimolecular process

$$CF_3I + HI \longrightarrow CF_3H + I_2$$

cannot occur to any extent under the experimental conditions.

Variation of CF_3I Pressure.

In order to find out if the reaction was now first order in CF_3I, a series of experiments were performed where the CF_3I pressure was varied. The results are listed in table 28 and are plotted in figure 57.

TABLE 28 Variation of CF_3I Pressure

Temperature = 249°C = 522°K Reaction Time = 3 hours =10,800 secs.

Expt. No.	Moles $CF_3I \times 10^4$	Pressure CF_3I (mms)	Moles HI $\times 10^4$	Equivs $I_2 \times 10^6$	Percent Decomp.
S15	1.71	7.95	121	82.5	24.0
S16	.86	4.0	52.4	29.8	17.3
S17	3.55	16.4	116	244	54.6
S18	4.30	20.0	118	338	39.3
S28	4.35	20.2	138	338	38.8
S29	.822	3.83	118	25.0	15.2

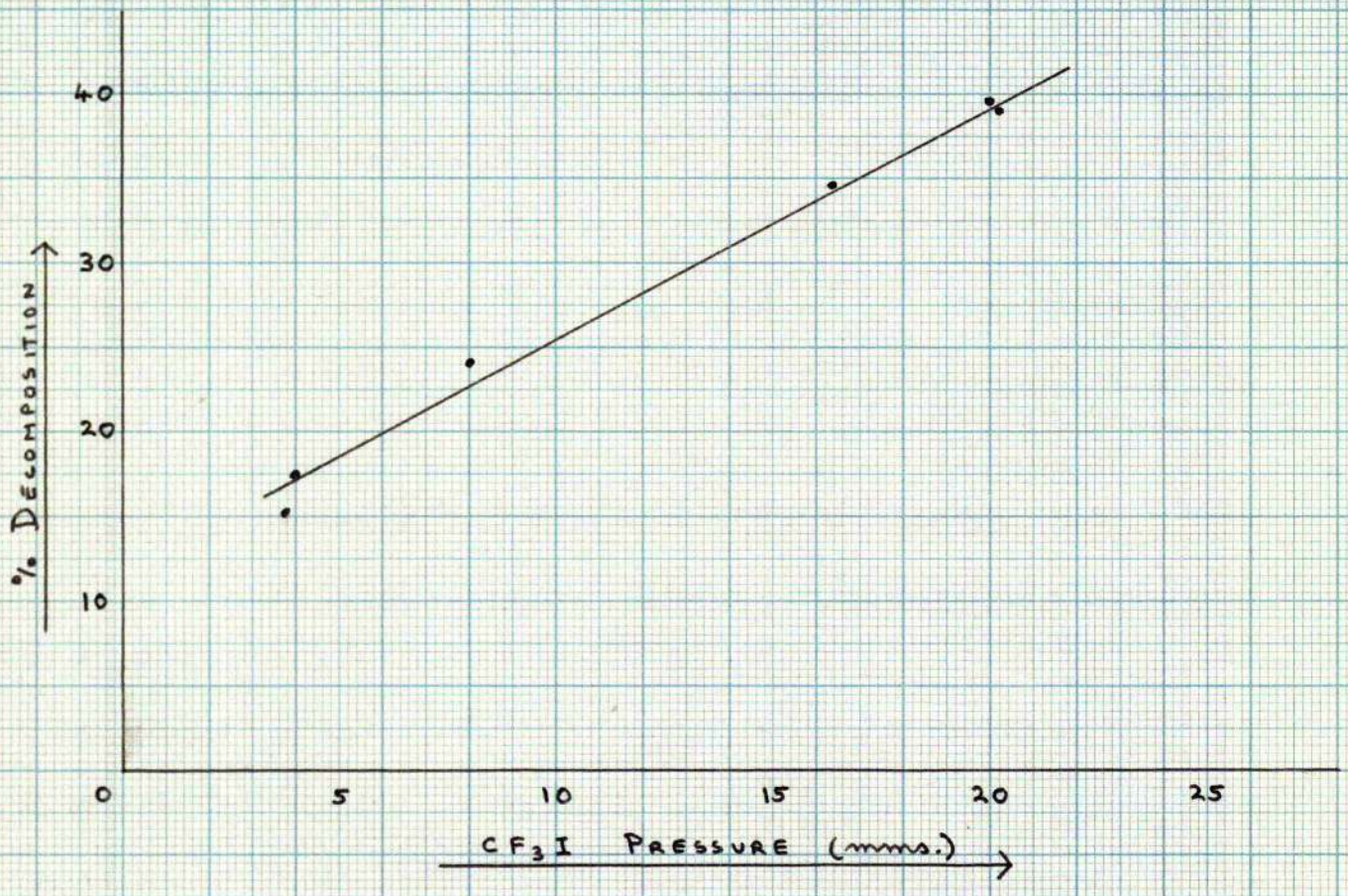
FIGURE 37 STATIC EXPERIMENTS

PERCENTAGE DECOMPOSITION OF CF_3I vs.

INITIAL CF_3I PRESSURE

522°K

REACTION TIME = 10,800 secs.



In evaluating the percentage decomposition, the iodine production from the HI has been ignored. This should not cause a serious error except perhaps in experiments S16 and S29 where the error may be about 10%. It is seen from figure 37 that the percentage decomposition is not independent of CF_3I pressure but that the reaction is between first and second order in CF_3I. Qualitative mass spectrometer analyses were performed on the liquid air condensable products of experiments S28 and S29. In experiment S29, only CF_3H was found, but in S28 a very little C_2F_6 was found as well; it was assumed that the stoichiometry was the same as in the flow system. At the time these experiments were performed, it was thought that this increase in rate constant with rise in CF_3I pressure might possibly still be due to the Hinshelwood-Lindemann effect, though it had been expected that the reaction would be first order in CF_3I at these pressures. The increase in percentage decomposition cannot be due to the bimolecular reaction

$$CF_3I + HI \longrightarrow CF_3H + I_2$$

for the rate has been found to be almost independent of HI pressure.

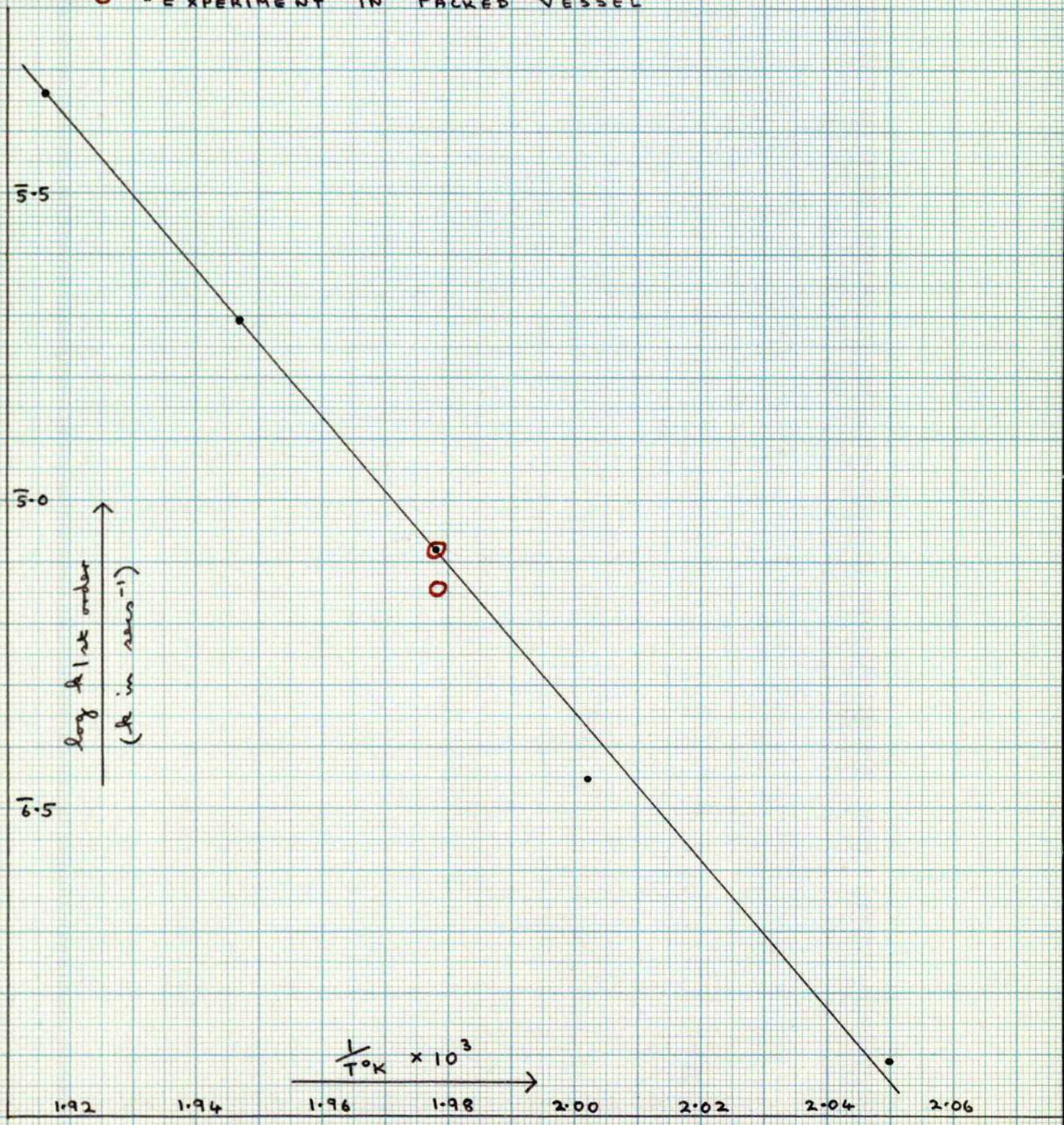
Temperature Coefficient and Alteration of Surface Area.

Since the rate now appeared to be much nearer first order than it had been in the flow system, it was decided to vary the temperature at a pressure of about 20 mms. of CF_3I and to examine the results as if the reaction were first order in CF_3I. The rate of reaction had been found to depend on the surface area in the flow system and this

FIGURE 38 STATIC EXPERIMENTS

LOG 1st order FOR DECOMPOSITION OF CF_3I vs $\frac{1}{T°K}$

○ = EXPERIMENT IN PACKED VESSEL



was examined under the sealed tube conditions. The change in the HI blank decomposition with temperature was also investigated. Table 29 contains a list of the results and log $k_{1st\ order}$ is plotted against the reciprocal of the absolute temperature in figure 38.

TABLE 29 Variation of Temperature and of Surface Area. Reaction Time = 3 hours = 10,800 secs.

Expt. No.	Moles $CF_3I \times 10^4$	Moles $HI \times 10^4$	Equivs $I_2 \times 10^6$ formed	$k_{1st\ order}$	log $k_{1st\ order}$	T (^oK)	$\frac{1}{T} \times 10^5$ (^oK)
S18	4.30	117	338	4.61×10^{-5}	$\bar{5}.6637$	522	1.916
S19	4.32	123	74	$.828 \times 10^{-5}$	$\bar{6}.9180$	505.5	1.978
S20	4.33	122	9.6	$.102 \times 10^{-5}$	$\bar{6}.0086$	488	2.049
S21	4.30	118	52.2	$.351 \times 10^{-5}$	$\bar{6}.5455$	499.5	2.002
S22	4.32	121	166	1.97×10^{-5}	$\bar{5}.2945$	515.5	1.947
*S25	4.26	120	63	$.712 \times 10^{-5}$	$\bar{6}.853$	505.5	1.978
*S24	4.26	121	73.5	$.852 \times 10^{-5}$	$\bar{6}.920$	505.5	1.978
S14	-	121	1.8	-	-	522	1.916
S25	-	16.7	1.8	-	-	507	1.972
S26	-	125	.35	-	-	488	2.049
S27	-	120	.55	-	-	505.5	1.978

$k_{1st\ order}$ is the assumed first order rate constant, in $secs^{-1}$

* indicates an experiment performed in a packed reaction vessel.

In experiment S25, the surface area was twice the normal area and in S24 it was three times greater than usual. In these experiments, the reaction vessels were packed with lengths of pyrex tubing the ends

of which had been fire polished. This packing of the reaction vessel appears to have had little effect on the rate of decomposition.

The amount of iodine produced by the decomposition of HI alone decreases with temperature and even in the worst case at 488°K, the amount of iodine produced by this method is only about 4% of the iodine produced when CF_3I is present. No correction has therefore been made for the iodine produced by the decomposition of HI in evaluating the rate constants.

From figure 38, the temperature dependence of the first order rate constant is found to obey the expression

$$k_{1st\ order} = 10^{18.9} \exp\left(\frac{-55,500}{RT}\right)$$

This value of $10^{18.9}$ for the temperature independent factor is considerably higher than the "normal" value of 10^{15} for a first order reaction. Admittedly, the justification for applying a first order equation (see figure 37) is far from strong and this high temperature independent factor tended to reinforce a growing doubt about the assumptions made up to this point. In particular, it suggested that the mechanism was not merely a split into CF_3 radicals and iodine atoms and subsequent suppression of the back reaction. On the other hand, the value for the activation energy = 55.5 K cals/mole is fairly close to the activation energies derived from the second order temperature coefficients in the flow system. These values ranged from 57.5 to 59.8 K cals/mole. It is also interesting that these values would be not unreasonable for $D(CF_3\text{-}I)$ which would be expected

to be near the value of $D(CH_3-I)$= 54.7 K cals/mole. Farmer, Henderson, Lossing and Marsden[60] derived $D(CF_3-I) = 57 \pm 4$ K cals/mole from electron impact work, and all these activation energies lie within this range.

However, when we considered the low values found for the efficiencies of the inert gases, the failure of the reaction to become first order even at 20 mms. pressure of CF_3I and the abnormal values found for the temperature independent factors, the suspicion deepened that the reaction mechanism must be more complex than had hitherto been suspected.

All of the findings mentioned above could have been obtained if the reaction was catalysed by the iodine produced due to the occurrence of the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

In particular, this would account for the rate being much higher than expected and producing an abnormally large temperature independent factor. There are two fairly simple methods of checking this. The reaction time can be varied in which case, if there is catalysis by iodine, the rate should increase as more iodine is produced at longer reaction times. Secondly, if the hypothesis is correct, addition of iodine should increase the rate of iodine production.

Variation of Reaction Time.

The results of these experiments are listed in table 30 and are plotted in figure 39.

FIGURE 39 STATIC EXPERIMENTS

PERCENTAGE DECOMPOSITION OF CF_3I

vs. REACTION TIME

499.5°K

4.30 & 4.35×10^{-4} MOLES CF_3I INITIALLY.

118 & 120×10^{-4} MOLES HI.

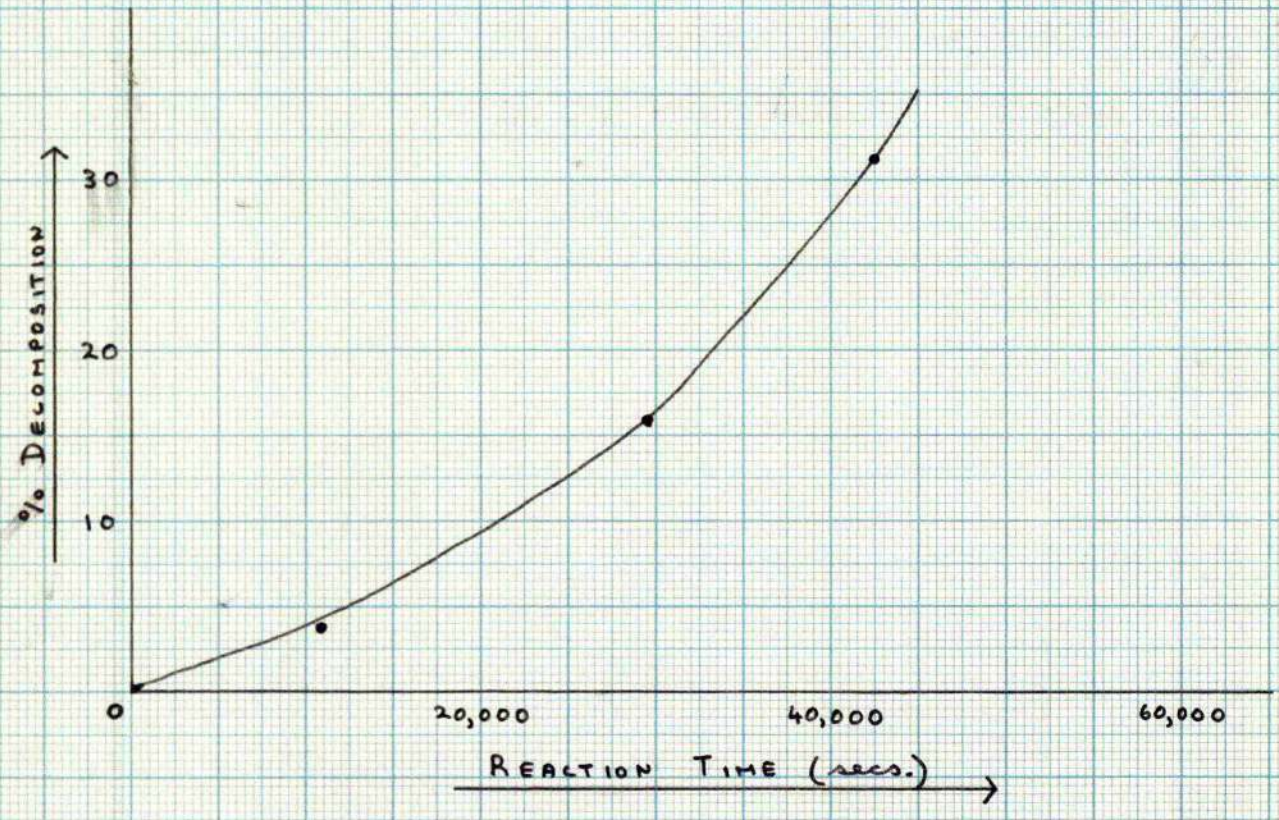


TABLE 30 Variation of Reaction Time

Temperature = 499.5°K

Expt. No.	Moles CF_3I x10^4	Moles HI x 10^4	Reaction Time (secs)	Percent Decomp.
S21	4.30	118	10,800	5.73
S30	4.35	120	29,580	15.95
S34	4.33	120	42,500	31.2

Figure 39 shows that the reaction is autocatalytic for the rate of production of iodine increases with reaction time.

Addition of Iodine.

In order to prove that iodine was causing the acceleration in rate, a series of experiments were performed in which iodine was added to constant amounts of CF_3I and HI. The results of this series are given in table 31. In experiments S38 and S39, the CF_3I concentration was varied.

FIGURE 40 STATIC EXPERIMENTS

PERCENTAGE DECOMPOSITION OF CF_3I vs.

IODINE ADDED.

488°K

REACTION TIME = 10,800 secs.

INITIAL CF_3I = 4·27 to 4·35 $\times 10^{-4}$ MOLES

HI = 118 to 125 $\times 10^{-4}$ MOLES

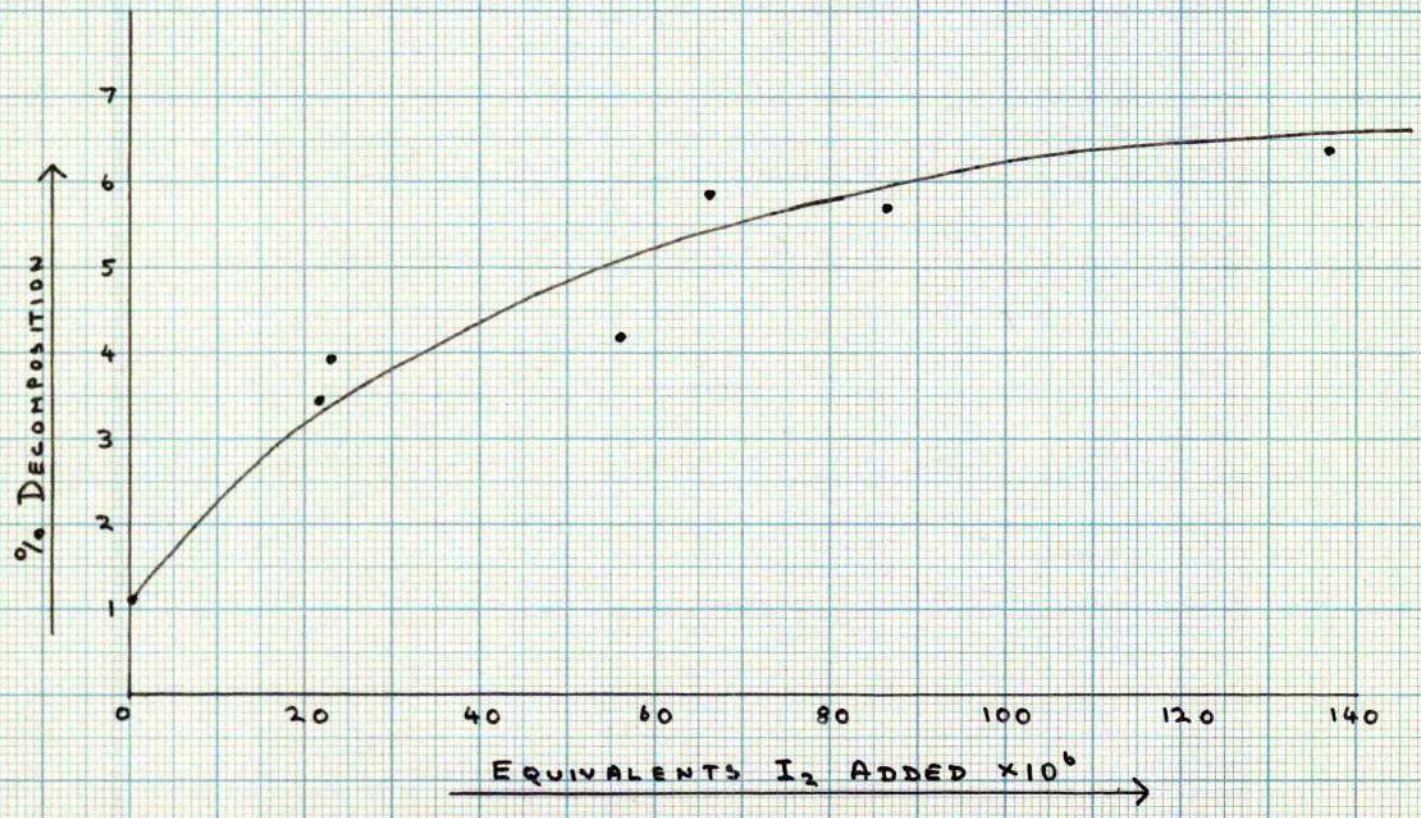


TABLE 31 Addition of Iodine

Temperature = 488°K. Reaction Time = 3 hours = 10,800 secs.

Moles HI in each experiment = 118 to 125 x 10^{-4}

Expt. No.	Moles $CF_3I \times 10^4$	Equivs I_2 added x 10^6	Equivs I_2 found x 10^6	Equivs I_2 made x 10^6	Percent Decomp.
S20	4.33	-	9.6	9.6	1.11
S31	4.35	22.7	57.0	34.5	3.95
S32	4.31	66.1	116.5	50.4	5.85
S33	4.33	86.5	136	49.5	5.7
S35	4.30	56.0	92.0	36.0	4.2
S36	4.32	137	191.0	54.0	6.35
S37	4.27	21.5	51.0	29.5	3.45
S38	2.16	57.5	72.0	14.5	3.35
S39	8.60	76.5	164	87.5	5.1

Figure 40 which is a plot of the percentage decomposition against the amount of iodine added for the experiments at a constant CF_3I pressure, shows that the rate is increased by addition of iodine. If the reaction causing this is

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

then the expression for the rate of formation of iodine should contain a term of the type

$$C_2 (I)(CF_3I)$$

where C_2 is related to the specific rate constants for the reaction steps.

The iodine atom concentration in units of gm.atoms/l is given by

$$(I) = \left[K_c(I_2)\right]^{\frac{1}{2}}$$

where K_c = equilibrium constant for dissociation of iodine in concentration units of gm. atoms/l. and moles/l. and where (I_2) is strictly the equilibrium concentration of iodine molecules. At the temperature and pressures used here, however, almost all the iodine is in the form of molecules, and it is a justifiable approximation to use (I_2) = total concentration of iodine. Thus the expression for the total rate of production of iodine should be of the form

$$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2'(CF_3I)(I_2)^{\frac{1}{2}}$$

where C_1 is a constant related to the specific rate constants and C_2' is related to C_2 by $C_2' = C_2K_c^{\frac{1}{2}}$.

At a constant CF_3I concentration, therefore, a plot of $\frac{d(I_2)}{dt}$ against $(I_2)^{\frac{1}{2}}$ should give a straight line of slope $C_2'(CF_3I)$ and making an intercept of $C_1(CF_3I)$ on the $(I_2)^{\frac{1}{2}} = 0$ axis. As for the flow system data, it is impossible to obtain values of $(I_2)^{\frac{1}{2}}$ and $\frac{d(I_2)}{dt}$ at any instant from the experimental results, but approximate mean values may be derived. The mean value of $\frac{d(I_2)}{dt}$ may be calculated. The initial $(I_2)^{\frac{1}{2}}$ and the final $(I_2)^{\frac{1}{2}}$ may also be found and the arithmetic mean is a good approximation for the effective mean $(I_2)^{\frac{1}{2}}$. These quantities have been calculated for the experiments at constant CF_3I concentration and are listed in table 32. No correction has been made for the slight changes in CF_3I concentration since the percentage decomposition changes only from 1% to 6.5%.

FIGURE 41 STATIC EXPERIMENTS

MEAN $(I_2)^{\frac{1}{2}}$ vs. MEAN $\frac{d(I_2)}{dt}$

488°K

CF_3I = 4·27 to 4·35 $\times 10^{-4}$ MOLES

HI = 118 to 125 $\times 10^{-4}$ MOLES

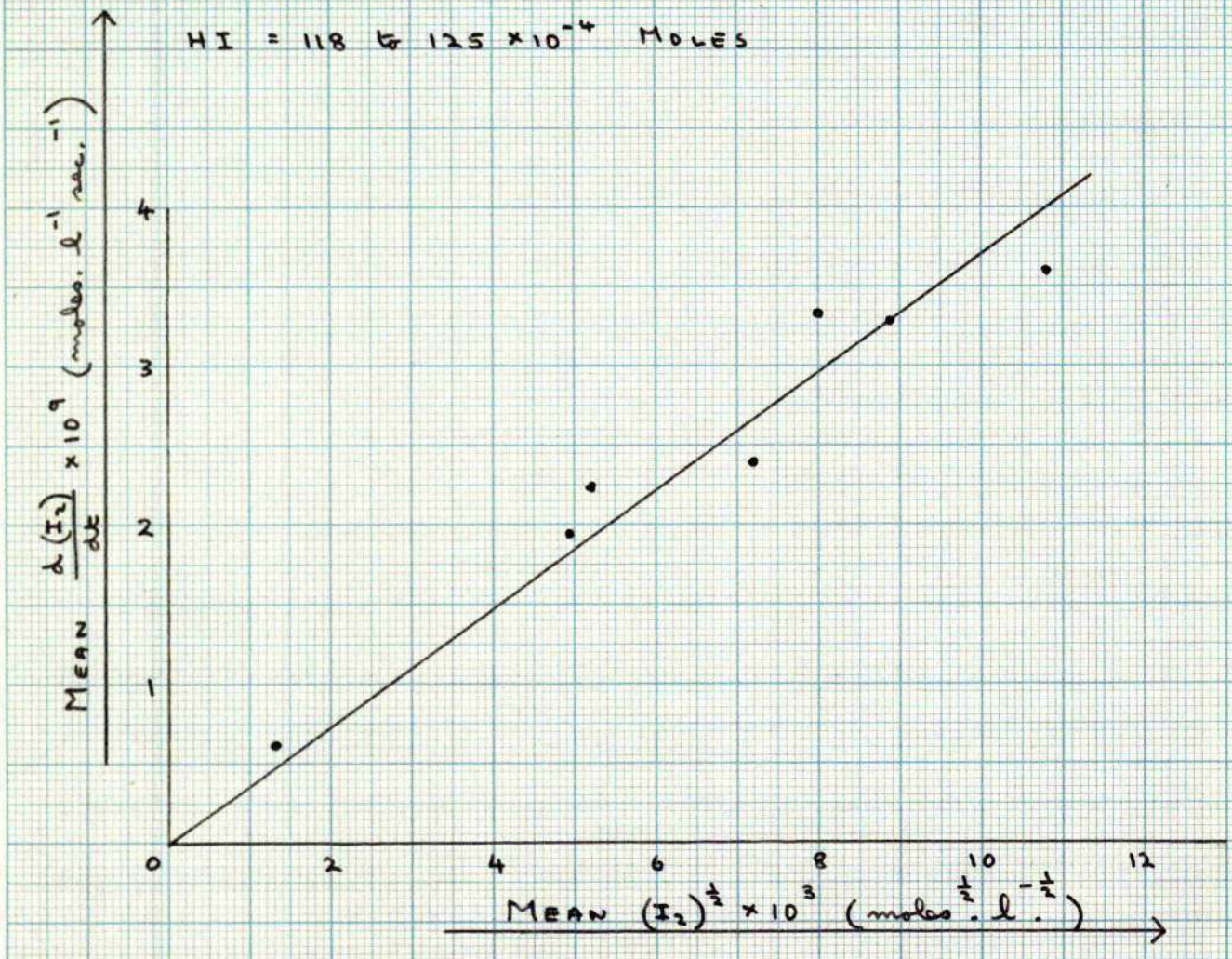


TABLE 32 Variation of $\frac{d(I_2)}{dt}$ with Mean $(I_2)^{\frac{1}{2}}$

Expt. No.	Initial $(I_2)^{\frac{1}{2}}$ moles$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$ x10^3	Final $(I_2)^{\frac{1}{2}}$ moles$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$ x10^3	Mean$(I_2)^{\frac{1}{2}}$ moles$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$ x10^3	Mean $\frac{d(I_2)}{dt}$ moles l^{-1} sec^{-1}
S20	0	2.62	1.31	.65 x 10^{-9}
S31	4.02	6.38	5.20	2.26 x 10^{-9}
S32	6.8	9.15	8.0	3.55 x 10^{-9}
S33	7.85	9.9	8.87	3.28 x 10^{-9}
S35	6.32	8.1	7.2	2.38 x 10^{-9}
S36	9.9	11.7	10.8	3.57 x 10^{-9}
S37	3.92	5.95	4.95	1.95 x 10^{-9}

In figure 41 is plotted $\frac{d(I_2)}{dt}$ against mean $(I_2)^{\frac{1}{2}}$ and it is seen that the experimental points lie approximately on a straight line which passes through the origin. The rate of production of iodine from the split of CF_3I must therefore be very small compared with the rate from the reaction step

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

From the slope of the line in figure 42, the value of C_2' is $6.0.10^{-4}$ $l^{\frac{1}{2}}$ moles$^{-\frac{1}{2}}$ sec^{-1}. This value of C_2' is only approximate since it has been produced using arithmetic means and was not derived from an integrated expression. If the iodine production from the initial split of CF_3I is ignored and if it is assumed that the iodine atom concentration is proportional to the (total iodine concentration)$^{\frac{1}{2}}$

then it is possible to derive an integrated expression from which to evaluate C_2'. The stoichiometric equation may be written

$$\underset{a-x}{CF_3I} + HI \longrightarrow \underset{x}{CF_3H} + \underset{x}{I_2}$$

where a = initial concentration of CF_3I in moles/l.

x = concentration of iodine in moles/l.

x = concentration of CF_3H in moles/l.

Then we have

$$\frac{dx}{dt} = C_2'(a-x)(x)^{\frac{1}{2}}$$

which may be integrated (appendix (iii)) to give

$$C_2' = \frac{2.303}{t\sqrt{a}}\left(\log\frac{\sqrt{a} + \sqrt{x}\text{ final}}{\sqrt{a} - \sqrt{x}\text{ final}} - \log\frac{\sqrt{a} + \sqrt{x}\text{ initial}}{\sqrt{a} - \sqrt{x}\text{ initial}}\right)$$

where t is the reaction time in seconds.

values of C_2' calculated in this way for all the experiments at 488°K are listed in table 53.

TABLE 53 Values of C_2' at 488°K

Expt. No.	S20	S51	S52	S53	S55	S56	S57	S58	S59
$C_2' \times 10^4$ ($l^{\frac{1}{2}}.moles^{-\frac{1}{2}}sec^{-1}$)	7.85	7.16	7.26	6.53	5.98	6.48	6.95	6.5	6.15

It is seen that the values of C_2' are fairly constant over the concentration ranges examined.

FIGURE 42 STATIC EXPERIMENTS

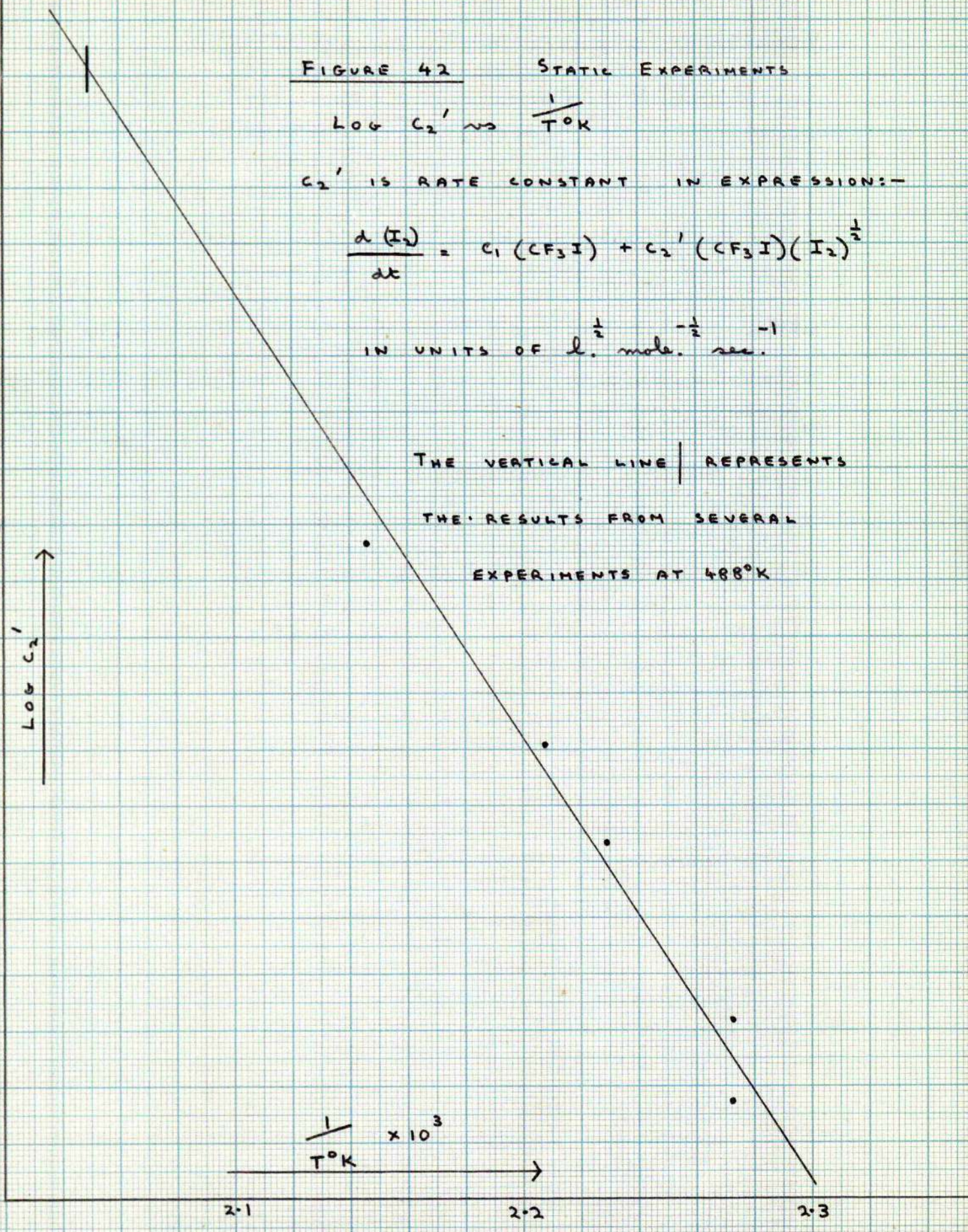
LOG C_2' vs $\frac{1}{T°K}$

C_2' IS RATE CONSTANT IN EXPRESSION:—

$$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2'(CF_3I)(I_2)^{\frac{1}{2}}$$

IN UNITS OF $l.^{\frac{1}{2}}\ mole.^{-\frac{1}{2}}\ sec.^{-1}$

THE VERTICAL LINE | REPRESENTS THE RESULTS FROM SEVERAL EXPERIMENTS AT 488°K



Variation of Temperature with the Addition of Iodine.

In order to obtain some idea of the activation energy for the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2$$

a series of experiments were performed where iodine was added at various temperatures. At 488°K, it has been shown that the rate of iodine formation from the split of CF_3I is negligible. This was the highest temperature used in the present work so that the rate of split of CF_3I might be neglected in all experiments. A high concentration of CF_3I was used and reactions were performed for long times in order to produce sufficient iodine for estimation. The results are given in table 54 and are plotted in figure 42.

TABLE 54. Variation of Temperature with Addition of Iodine.
Moles CF_3I used = 8.58 to 8.70 10^{-4} moles. Moles HI = 115 to 125.10^{-4}

Expt. No.	Equivs I_2 put in x 10^6	Equivs I_2 found x 10^6	Reaction Time (secs)	C_2' x 10^5 $l.^{\frac{1}{2}}mole^{-\frac{1}{2}}sec^{-1}$	log C_2'	T (°K)	$\frac{1}{T}$ x10^3
S40	58.8	53.7	38,400	4.06	$\bar{5}.610$	455	2.208
S41	58.7	79.0	37,800	9.26	$\bar{5}.967$	466	2.146
S42	26.2	42.5	72,600	2.72	$\bar{5}.435$	449	2.229
S43	59.8	58.5	144,000	1.32	$\bar{5}.121$	440	2.275
S44	52.9	81.0	259,200	.944	$\bar{6}.975$	440	2.275
				59.8 to 78.5	$\bar{4}.777$ to $\bar{4}.861$	488	2.049

The slope of the line in figure 42 is 36.4 K cals/mole. The activation energy E of the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2$$

is related to this value of 36.4 K cals/mole by the expression

$$E = 36.4 - \tfrac{1}{2} D(I\text{-}I)$$

At 475°K, D (I-I) = 36.4 K cals/mole.

$$\therefore E = 36.4 - 18.2 = \underline{18.2 \text{ K cals/mole.}}$$

The implications of these experiments and their relation to other data are treated in the discussion section.

* * * * * * *

DISCUSSION.

Summary.

In the experimental section, evidence has been presented which shows the following features in the pyrolysis of CF_3I.

(a) In the presence of low pressures of an inert carrier gas and in the absence of any radical acceptors the decomposition produced essentially C_2F_6 and I_2. The rate of decomposition under these circumstances decreased rapidly with increase in the percentage of reaction.

(b) The addition of toluene and HI as radical acceptors increased the percentage decomposition of CF_3I under given conditions. With toluene the products were complicated, but C_2F_6 formation was largely suppressed in favour of CF_3H. With HI, conditions could be obtained where there was no observable C_2F_6.

(c) Under conditions where the rate was independent of HI pressure, the rate of iodine production was between first and second order in CF_3I concentration. At low pressures in the flow system there was a slight inert gas effect and the rate of reaction was affected by the surface area.

(d) In the presence of sufficient HI, the reaction was found to be catalyzed by the addition of iodine under all conditions examined, and in some circumstances this iodine catalyzed reaction was the main source of iodine production.

In the experimental section, some discussion of the reaction was given in order to show why various series of experiments were performed. The results may now be discussed more fully in the light of further experimental evidence obtained, especially that mentioned in (d) above.

In the following discussion, the numbering which was applied to the reaction steps in the experimental section is used.

The Pyrolysis of CF_3I Alone.

In the experimental section, it was shown that the stoichiometric equation for the reaction under these conditions approximated very closely to

$$2\,CF_3I \longrightarrow C_2F_6 + I_2$$

To account for the observed fall off in rate as the percentage decomposition increased, the reaction was interpreted as proceeding by the steps:-

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

$$CF_3 + I \longrightarrow CF_3I \qquad (2)$$

$$I + I \rightleftharpoons I_2 \qquad (3)$$

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (4)$$

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (5)$$

As a result of the evidence summarised briefly in paragraph (d) above, it is now known that reaction (14)

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

must also have occurred. The amount of iodine builds up as the reaction proceeds and therefore more CF_3 radicals react by reactions (2) and (4) to reform CF_3I; this is the cause of the decrease in rate. No direct evidence was obtained for reactions (2) and (4) by injecting iodine. The occurrence of these reactions has been proved indirectly by the addition of toluene and of hydrogen iodide. In the presence of both of these compounds the percentage decomposition was greatly increased, CF_3H was formed and the formation of C_2F_6 was reduced. This increase in decomposition and the change in the nature of the products is most readily explained as being due to the suppression of reactions (2) and (4).

Thus, in the system, there are three pairs of opposing reactions

$$CF_3I \rightleftharpoons CF_3 + I \qquad (1) \text{ and } (2)$$

$$CF_3I + I \rightleftharpoons CF_3 + I_2 \qquad (4) \text{ and } (14)$$

$$I + I \rightleftharpoons I_2 \qquad (3)$$

It would therefore seem reasonable to consider that the removal of CF_3 radicals in reaction (5)

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (5)$$

causes the reaction to proceed. The lowest estimate of $D(F_3C\text{-}CF_3)$ in the literature is 62 K cals/mole[55] so it is unlikely that the reverse of reaction (5)

$$C_2F_6 \longrightarrow CF_3 + CF_3$$

will take place under the reaction conditions.

From measurements of the rate of recombination of CF_3 radicals

at 400°K, it has been calculated that if the steric factor for the reaction is unity, then the activation energy for the reaction is 1.5 K cals/mole or that if the activation energy is zero, then the steric factor is 0.16[57]. Reaction (5) has been found to be independent of total pressure down to 0.5 mms.[61] Under the experimental conditions, therefore, it is possible that the rate of collision of CF_3 radicals might be the factor which controls the rate of decomposition.

It is difficult to decide from the available data whether the main back reaction is

$$C F_3 + I \longrightarrow C F_3 I \qquad (2)$$

or

$$C F_3 + I_2 \longrightarrow C F_3 I + I \qquad (4)$$

Reaction (2) will have a negligible activation energy but will almost certainly require a third body. However, as this work was done at a pressure where reaction (1)

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

is almost first order in CF_3I, third body considerations should not be important. Reaction (4) will have a small activation energy, probably not more than 2 K.cals/mole but this should not be important at the temperature used in this work. Both reactions will occur in the present system.

The products could also be accounted for by the bimolecular process

$$C F_3 I + C F_3 I \longrightarrow C_2 F_6 + I_2$$

The kinetics cannot be explained by this mechanism, however, and since the production of C_2F_6 can be stopped completely by the addition of sufficient HI, this bimolecular reaction does not occur under the conditions examined. It can be concluded therefore that the decomposition proceeds completely by a free radical mechanism. It is interesting to speculate upon the possible reasons for the non occurrence of the bimolecular reaction. It has been tentatively suggested by Hirschfelder[105] that the activation energy of a bimolecular reaction is 28% of the sum of the two bonds being broken. If we take $D(CF_3\text{-}I)$ = 54 K. cals/mole., this gives an activation energy for the bimolecular reaction of 30 K.cals/mole. If we assume a "normal" pre-exponential factor for the bimolecular reaction of 10^{11} l.mole^{-1} sec^{-1}, we have that at 800°K and a CF_3I concentration of 5.10^{-6} moles/l (= 0.25 mms), a rate of formation of iodine given by

$$\frac{d(I_2)}{dt} = 10^{11}\ 10^{\frac{-30,000}{4.57.800}}\ .25.10^{-12}$$

$$= 2.5.10^{-8}\ \text{moles.l}^{-1}\text{sec}^{-1}$$

The actual rate of formation of iodine under these circumstances was of the order of 10^{-7} moles.l^{-1}sec^{-1}, so, from the above calculation, it would appear that the bimolecular reaction should give an appreciable amount of the iodine formed. However, if the reaction were to have a steric factor of 10^{-2} or less, the amount of iodine produced from the bimolecular reaction would be negligible compared with that from the free radical process. There is in the literature theoretical[6] and experimental[8, 106] evidence which suggests that a

reaction of this type might have a steric factor several powers of ten smaller than 10^{-2}. The experimental results obtained in this investigation show that the reaction does not take place, and its non occurrence must presumably be due to there being a steric factor of 10^{-2} or less if the approximate calculations about the activation energy for the reaction are reasonably correct.

The process $C F_3 + C F_3 I \longrightarrow C_2 F_6 + I$

could also account for the reaction products. The evidence against the occurrence of this reaction is that the rate of decomposition is not dependent on CF_3I pressure and is, in fact, increased when CF_3 radicals are removed by toluene or hydrogen iodide. Hirschfelder[105] has suggested that the activation energy for an exothermic reaction of the type

$$A + B C \longrightarrow A B + C$$

is 5% of the bond energy D(B-C). This is obviously not very accurate for it is now known that the activation energies for such reactions vary with the nature of the attacking radical A However, in many cases, the rule does give an activation energy of the correct order of magnitude. Using a value of $D(CF_3-I)$ = 54 K.cals/mole, the reaction

$$C F_3 + C F_3 I \longrightarrow C_2 F_6 + I$$

might have an activation energy of about 2.7 K.cals/mole.

It is doubtful if the Hirschfelder rule is really applicable in this case. The actual reaction will involve inversion about the carbon atom of the CF_3I molecule and because of this, the reaction may

have an activation energy considerably greater than the approximate value derived above. The process may also be sterically difficult. A CF_3 radical is probably planar and a CF_3I molecule is tetrahedral in shape. The most favourable position for attack by the CF_3 radical will be along the line of the carbon-iodine bond. The hydrogen abstraction reactions by methyl radicals[8,9] require rather similar steric conditions and for these reactions the steric factor is of the order of 10^{-3} to 10^{-4}. In this case, therefore, the steric factor will certainly not be greater than 10^{-4}. These factors, together with the low concentration of reactants, are probably the reasons for the non occurrence of the reaction.

The data obtained are not of very high accuracy and it would be interesting to examine the reaction in a vessel completely unattacked by the products. Under these conditions, it might be possible to determine whether the reaction

$$C F_3 + C F_3 \longrightarrow C_2 F_6 \qquad (5)$$

is in fact the rate determining step.

The Reaction in the Presence of Toluene.

In the presence of toluene, the products found were I_2, $C_6H_5CH_2I$, HI, C_2F_6, CF_3H, $C_6H_5CH_2CH_2C_6H_5$ and $C_6H_5CH = CHC_6H_5$. The experiments with toluene in the nickel vessel are not sufficiently extensive or systematic to make any quantitative deductions. They do show, however, that CF_3 radicals are involved in the reaction and that toluene increases the rate of decomposition by removing CF_3

radicals to form CF_3H and thus prevent the back reaction. The production of dibenzyl and stilbene shows that the benzyl radicals produced in the reaction

$$C F_3 + C_6 H_5 C H_3 \longrightarrow C F_3 H + C_6 H_5 C H_2 \qquad (6)$$

dimerise as would be expected.

In the much more extensive work in the pyrex vessel, it was shown that benzyl iodide and hydrogen iodide were formed due to the reactions of iodine with toluene. Hydrogen iodide had been found by Alexander[86] in an investigation on the reaction of iodine with toluene but he found no benzyl iodide at the rather higher temperatures he used. The following scheme was suggested in the experimental section to account for the formation of all the products found:-

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

$$I + C F_3 \longrightarrow C F_3 I \qquad (2)$$

$$I + I \rightleftharpoons I_2 \qquad (3)$$

$$C F_3 + I_2 \longrightarrow C F_3 I + I \qquad (4)$$

$$C F_3 + C F_3 \longrightarrow C_2 F_6 \qquad (5)$$

$$C F_3 + C_6 H_5 C H_3 \longrightarrow C F_3 H + C_6 H_5 C H_2 \qquad (6)$$

$$2 C_6 H_5 C H_2 \longrightarrow C_6 H_5 C H_2 C H_2 C_6 H_5 \qquad (7)$$

$$C_6H_5CH_2CH_2C_6H_5 + 2CF_3 \longrightarrow C_6H_5CH = CHC_6H_5 + 2 CF_3H \qquad (8)$$

$$C_6H_5CH_2CH_2C_6H_5 + 2I \longrightarrow C_6H_5CH = CHC_6H_5 + 2 HI \qquad (9)$$

$$C_6 H_5 C H_2 + I \longrightarrow C_6 H_5 C H_2 I \qquad (10)$$

$$C_6 H_5 C H_2 + I_2 \longrightarrow C_6 H_5 C H_2 I + I \qquad (11)$$

$$C_6 H_5 C H_3 + I \longrightarrow C_6 H_5 C H_2 + H I \qquad (12)$$

It is now known that the reaction would be iodine catalyzed so reaction (14) must also have taken place

$$I + C F_3 I \longrightarrow C F_3 + I_2 \qquad (14)$$

It has also been shown that HI reacts very readily with CF_3 radicals, so, although it is present only in small concentration, the reaction

$$C F_3 + H I \longrightarrow C F_3 H + I \qquad (15)$$

will probably proceed as well.

Reactions (8) and (9) proceed in stepwise fashion

$$R + C_6 H_5 C H_2 C H_2 C_6 H_5 \longrightarrow R H + C_6 H_5 C H_2 C H C_6 H_5$$

$$R + C_6 H_5 C H_2 C H C_6 H_5 \longrightarrow R H + C_6 H_5 C H = C H C_6 H_5$$

where R = $C F_3$ or I.

It is also possible for the radical

$C_6 H_5 C H_2 C H C_6 H_5$ to decompose and to yield a hydrogen atom:-

$$C_6 H_5 C H_2 C H C_6 H_5 \longrightarrow C_6 H_5 C H = C H C_6 H_5 + H.$$

This H atom may then react with toluene to produce H_2 or CH_4 according to:-

$$H + C_6 H_5 C H_3 \longrightarrow C_6 H_5 C H_2 + H_2$$

$$\text{or} \quad H + C_6 H_5 C H_3 \longrightarrow C_6 H_5 + C H_4$$

The small amount of benzene which would be formed by the phenyl radical was not detected, but it is probably this mechanism which accounts for the traces of H_2 and CH_4 found in the carrier gas.

The increase in the rate of reaction as the toluene pressure is increased at constant CF_3I pressure is presumably due to more CF_3

radicals reacting by process (6)

$$C F_3 + C_6 H_5 C H_3 \longrightarrow C F_3 H + C_6 H_5 C H_2 \qquad (6)$$

and less back reaction taking place.

The decrease in percentage decomposition with reduction in CF_3I pressure at constant toluene pressure was at the time interpreted as being wholly due to the Hinshelwood Lindemann effect, but it is really due to two causes. Firstly, there is this decrease in rate which occurs with any unimolecular reaction as the pressure is lowered and secondly, at lower pressures, both the iodine and CF_3I concentrations are smaller, so reaction (14)

$$I + C F_3 I \longrightarrow C F_3 + I_2 \qquad (14)$$

will not proceed so readily. The free iodine concentration is very much reduced at these low pressures since so much reacts with the toluene. C_2F_6 is formed in these experiments, so all the CF_3 radicals cannot react with the toluene. Since the concentrations of I atoms and I_2 molecules are higher than the concentration of CF_3 radicals, it follows that some back reaction must occur by

$$C F_3 + I \longrightarrow C F_3 I \qquad (2)$$

and

$$C F_3 + I_2 \longrightarrow C F_3 I + I \qquad (4)$$

It is therefore not possible to evaluate the rate of formation of iodine due to process (1)

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

or process (14)

$$I + C F_3 I \longrightarrow C F_3 + I_2 \qquad (14)$$

because of this occurrence of the back reactions. Nevertheless, the approximate ratio of rates of formation of iodine may be calculated from data obtained using HI when all the CF_3 radicals were caught. By extrapolation of the data on the temperature coefficient of the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

it is possible to derive the rate constant for this reaction

$$C_2 = 1.09 \times 10^6 \text{ l mole}^{-1}\text{sec}^{-1} \text{ at } 797^\circ K$$

(figure 45). On page [81] it is derived that the temperature dependence of the rate of initial split of CF_3I is given by

$$k = 10^{14.3} \exp \frac{-55,500}{RT} \text{ secs}^{-1}$$

This expression will not be very accurate but it yields

$$k = .40 \text{ secs}^{-1} \text{ at } 797^\circ K \text{ for } CF_3I \longrightarrow CF_3 + I$$

It is therefore now possible to calculate the relative rates of formation of iodine by these two processes using the arithmetic mean concentrations and assuming that the rate of split of CF_3I remains first order over the pressure range examined. The results of the calculations are given in table 55, average values for the experiments being quoted.

TABLE 35 Ratio of Rates of formation of Iodine

Expt No.	Mean (I) $\times 10^8$ gm. atoms /l.	Mean(CF_3I) $\times 10^6$ moles/l	Mean $\frac{d(I_2)}{dt}$ catalytic $\times 10^7$ moles $l^{-1} sec^{-1}$	Mean $\frac{d(I_2)}{dt}$ split $\times 10^7$ moles $l^{-1} sec^{-1}$	$\frac{I_2 \text{ catalytic}}{I_2 \text{ total}}$ (per cent)
52	11.5	8.20	10.5	35.0	24
51	8.5	5.20	4.81	21.0	18.6
27	7.3	4.32	3.44	17.3	16.4
33	5.64	3.31	2.04	15.2	13.1
34	5.78	2.24	.925	8.95	9.4
35	2.24	1.61	.393	6.45	5.8
36	1.57	1.18	.202	4.7	4.1
37	.302	.56	.0184	2.24	.80
38	.183	.45	.0085	1.71	.53
39	.282	.57	.0104	1.48	.67

The mean (I) is the mean concentration of free iodine atoms.

"Catalytic" refers to the process

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

and "split" to the reaction

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

Table 35 shows that the catalytic reaction accounts for almost one quarter of the iodine formed at the highest pressure of CF_3I used, but that at the low pressures, the rate of production of iodine due to this reaction is negligible. The shape of the experimental curve

produced in figure 21 is therefore due to several reasons. From the rather approximate calculations presented in table 35 it is seen that the reduction of the catalytic reaction as the CF_3I pressure is lowered would reduce the percentage decomposition from 10.5% to 7.9%. The decomposition actually falls from 10.5% to about 6% with lowering of the CF_3I concentration. The rest of the decrease is probably due to the falling off in rate of split of CF_3I at the very low pressures used, but it is difficult to assess the importance of this effect in the present system which is complicated by the failure of the toluene to react with all the CF_3 radicals.

It is interesting to note that under conditions where all the CF_3 radicals reacted with toluene, an increase in total rate could be produced by lowering the toluene pressure and thus decreasing the amount of hydrogen iodide and benzyl iodide formed. This would increase the extent of the catalytic reaction and hence would raise the percentage decomposition.

The small increases in rate found by raising the pressures of nitrogen and argon must presumably be due to the rate of initial split not being first order in CF_3I pressure. However, since the exact order of reaction is not known and since back reaction occurs, it is not possible to make any quantitative deductions about the efficiencies of these gases in transferring energy. Raising the inert gas pressure has the effect of impeding diffusion to the wall, but will not affect the relative number of collisions a CF_3 radical

will make with toluene and iodine.

The failure to account for all the CF_3 radicals in the experiments where CF_3H and C_2F_6 were estimated has been discussed to some extent in the experimental section. The most likely solution is that $C_6H_5CH_2CF_3$ was formed but a small amount of the CF_3 radicals would also decompose to give carbon on the walls of the reaction vessel.

The failure of toluene to react with all the CF_3 radicals would imply that the reaction

$$CF_3 + C_6H_5CH_3 \longrightarrow CF_3H + C_6H_5CH_2 \qquad (6)$$

has either an appreciable activation energy or a very low steric factor. It is possible to calculate ΔH for the reaction from available data.

$\Delta Hf\ (CF_3) = -119$ K cals./mole[55,60,65]

$\Delta Hf\ (PhCH_3) = +11.9$ K cals./mole[107]

$\Delta Hf\ (CF_3H) = -169$ K cals./mole[108,65]

$\Delta Hf\ (PhCH_2)$. There is some disagreement here. Benson and Buss[109] list values ranging from 34 to 50 K cals./mole. They favour a value of 44 K cals./mole which is also supported by Alexander[86] and Gow[29] Using $\Delta Hf\ (PhCH_2) = 44$ K cals./mole, this gives ΔH for reaction (6) = -18 K cals./mole. Thus the reaction is exothermic and there is no activation energy on account of endothermicity.

Using the approximate rule stated by Hirschfelder[105] and taking $D(C_6H_5CH_2\text{-}H) = 84$ K cals./mole we have that the activation energy for

reaction (6)

$$CF_3 + C_6H_5CH_3 \longrightarrow CF_3H + C_6H_5CH_2 \qquad (6)$$

is about 4 K cals./mole.

It is also possible to estimate the activation energy of reaction (6) from a knowledge of the activation energy of the reaction

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \qquad (6a)$$

Values of the activation energy of reaction (6a) range from 7 ± 2 to 11 ± 2 K cals./mole[110,111,112,10]; a reasonable mean value would be of the order of 9 K cals./mole. It has been shown[56,59] that activation energies for hydrogen abstraction reactions of CF_3 radicals are about 2 to 5 K cals./mole lower than the activation energies for analogous reactions of CH_3 radicals. This would make the activation energy of reaction (6) about 6 or 7 K cals./mole. This value is higher than the approximate value from the Hirschfelder equation and is probably more accurate.

At 800° K under the reaction conditions most of the iodine is dissociated into atoms and we could consider that reaction (2)

$$CF_3 + I \longrightarrow CF_3I \qquad (2)$$

is the main CF_3I reforming reaction. If we assume that the activation energy for reaction (6) is 6 K cals./mole and if it is taken that the pre exponential factors for reactions (2) and (6) are the same, then the ratio of k_2/k_6 at 800°K is given approximately by

$$\frac{k_2}{k_6} = 10^{\frac{6,000}{800.4.57}} = 10^{1.6} = 40$$

Thus, if all the assumptions are correct, it would be necessary to have a toluene concentration 4,000 times the iodine concentrations in order that only 1% of the CF_3 radicals should reform CF_3I. The highest ratio which was actually achieved was $PhCH_3$: I = 1,400:1 in experiment 39 so that even in this case, some back reaction might occur.

From figure 25 it was possible to derive that at 797°K, the ratio

$$\frac{k_6}{k_5^{\frac{1}{2}}} = 128\ l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-\frac{1}{2}}$$

$$C F_3 + C F_3 \xrightarrow{k_5} C_2 F_6 \qquad (5)$$

$$C F_3 + C_6H_5CH_3 \xrightarrow{k_6} C F_3 H + C_6H_5 C H_2 \qquad (6)$$

Since no information was obtained on the temperature dependence of this ratio, a value of the activation energy cannot be obtained without making an assumption about the temperature independent factor of reaction (6). Although the collision frequency of CF_3 and $PhCH_3$ could be evaluated reasonably accurately, the steric factor is unknown. An activation energy of the order of a few K.cals/mole derived from a rate constant at one temperature is very sensitive to the value of the pre-exponential factor chosen and we do not consider it profitable to pursue this point. Thus no value can be derived from this work.

It is not impossible that a bimolecular reaction

$$C F_3 I + Ph C H_3 \longrightarrow C F_3 H + Ph C H_2 I$$

or

$$C F_3 I + Ph C H_3 \longrightarrow Ph C H_2 C F_3 + H I$$

might occur. However, the decomposition is independent of CF_3I concentration under some conditions and the results can all be explained by a free radicals mechanism, so it would appear that these reactions do not proceed under the conditions used.

The Reaction in the Presence of Hydrogen Iodide.

The experiments performed using hydrogen iodide to capture the CF_3 radicals give much more quantitative information than did the work with toluene. When sufficient HI is added, the rate of reaction is independent of HI pressure and the products are CF_3H and I_2 only. In the knowledge that the reaction was iodine catalyzed, the reaction may now be represented as occurring by the following reaction steps:-

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

$$I + I \rightleftharpoons I_2 \qquad (2)$$

$$CF_3 + HI \longrightarrow CF_3H + I \qquad (15)$$

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

Reaction (15) is the only process by which CF_3 radicals react. It is possible to treat this series of reaction steps in such a manner as to produce a rate expression similar to the experimentally derived

$$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2(CF_3I)(I)$$

Assuming that a small stationary concentration of CF_3 radicals is produced and that the rate of initial split of CF_3I is first order, we have

$$(CF_3) = \frac{k_1 (CF_3I) + k_{14}(I)(CF_3I)}{k_{15} (HI)}$$

The total rate of formation of iodine in gm. atoms.l^{-1}sec^{-1} is given by

$$\frac{d (I)}{dt} = k_1(CF_3I) + k_{15}(CF_3)(HI) + k_{14}(I)(CF_3I)$$

$$= 2\, k_1(CF_3I) + 2\, k_{14}(I)(CF_3I)$$

Therefore, the total rate of formation of iodine in gm.moles.l^{-1}sec.$^{-1}$ is given by

$$\frac{d (I_2)}{dt} = k_1(CF_3I) + k_{14}(I)(CF_3I)$$

On comparing this with the experimentally produced expression, it is seen that $C_1 = k_1$ and $C_2 = k_{14}$.

Before the experiments using HI were commenced, it was feared that there might be a bimolecular reaction

$$CF_3I + HI \longrightarrow CF_3H + I_2$$

There are, as have already been mentioned, two pieces of published evidence about the use of HI as a radical acceptor and these may now be examined in the light of the results obtained in this investigation.

In his investigations on the thermal reactions of methyl, ethyl and n-propyl iodides with HI, Ogg[58] obtained results which he interpreted as being due partly to the reactions

$$RI + HI \longrightarrow RH + I_2$$

where R = methyl, ethyl or n-propyl. However, the greatest ratio of HI : RI which he used was 5.7:1 and many experiments were performed where the ratio HI:RI was less than 1:1. He allowed the reactions

to proceed until at least 50% of the reactant in smaller concentration was consumed. If the behaviour of the iodides he examined is similar to the behaviour of CF_3I, the conditions would not be such that all the radicals reacted with HI. The rate would then depend on HI concentration and it is possible that this effect might have been interpreted as being due to a bimolecular reaction.

Iredale and Stephan[18] investigated the photolysis of CH_3I - HI mixtures and found a quantum yield of about 2 when the mixture contained from 40% to 88% of HI. Thus no bimolecular reaction occurred under their conditions at 17°C to 20°C. The relative concentrations of reactants which they used are similar to the ratios employed in this work and the results they obtained are of the same pattern; similar interpretations have been put forward in each case.

In the present investigation, it was shown that above a certain limit, the pressure of HI had no effect on the rate of reaction, and so the bimolecular process

$$CF_3I + HI \longrightarrow CF_3H + I_2$$

did not occur to any extent under the conditions examined. The data in the sealed tubes are not as conclusive as the data from the flow system in this respect, but the static experiments were complicated by the slight decomposition of HI alone.

In view of these findings, it would be interesting to examine the thermal decomposition of CH_3I - HI mixtures where the HI : CH_3I ratio was varied up to about 100 : 1 and the decomposition restricted to

say 10% of the CH_3I.

Using the empirical Hirschfelder rule[105] that the activation energy of a bimolecular reaction is 28% of the sum of the bonds being broken, we obtain that E for the reaction

$$CF_3I + HI \longrightarrow CF_3H + I$$

$$= 28\% \text{ of } \left[D(CF_3\text{-}I) + D(H\text{-}I)\right]$$

$$= 28\% \text{ of } \left[54 + 71\right]$$

$$= \underline{35 \text{ K cals./mole}}$$

If we use this approximate activation energy of 35 K cals./mole and if we assume that the temperature independent factor for the rate constant has a "normal" value of 10^{11}, then for a CF_3I concentration of 5.10^{-6} moles/l (.24 mms) and an HI concentration of 5.10^{-5} moles/l (2.4 mms) we would have at 760°K a rate of iodine formation given by

$$\frac{d(I_2)}{dt} = 10^{11} \cdot 10^{\frac{-35,000}{4.57 \cdot 760}} \cdot .25 \cdot 10^{-11}$$

$$= 25.10^{-10} \text{ moles.l.}^{-1}\text{sec.}^{-1}$$

The actual rate of formation of iodine under these conditions was of the order of 10^{-6} moles $l^{-1}sec^{-1}$ so the bimolecular reaction would produce less than 1% of this amount even if the steric factor for the reaction was unity.

Under static reaction conditions, if we assume an HI concentration of $1.5.10^{-2}$ moles/l and a CF_3I concentration of 10^{-5} moles/l, we would have at 500°K a rate of iodine formation given by

$$\frac{d(I_2)}{dt} = 10^{11} \cdot 10^{\frac{-35,000}{4.57 \cdot 500}} \cdot 1.5 \cdot 10^{-5}$$

$$= 1.5.10^{-9} \text{ moles.l.}^{-1}\text{sec.}^{-1}$$

The experimental rate of iodine formation under these conditions is of the order of 10^{-8} moles $l^{-1} sec^{-1}$. The bimolecular reaction might therefore seem to be an appreciable source of iodine production in these circumstances. However, from theoretical calculations[6], it has been derived that the steric factor for the reaction of a diatomic molecule with a polyatomic molecule will be between 10^{-4} and 10^{-8}. It is fairly well established[8] that the steric factor for the reaction of a radical with a molecule is of the order of 10^{-4}, so this estimate is not unreasonable. Therefore, it is very likely that the reaction

$$C F_3 I + H I \longrightarrow C F_3 H + I_2$$

will have a steric factor of this magnitude in which case the contribution from this reaction will be negligible in all experiments performed.

Since HI reacts so much more efficiently with CF_3 radicals than did toluene, the rate constant for the reaction

$$C F_3 + H I \longrightarrow C F_3 H + I \qquad (15)$$

must be much greater than the rate constant for the reaction

$$C F_3 + C_6 H_5 C H_3 \longrightarrow C F_3 H + C_6 H_5 C H_2 \qquad (6)$$

under the same conditions.

It is probable that the steric factor for reaction (6) is less than for reaction (15) but the main cause of the difference in rates is more likely to be due to the difference in activation energies of the reactions. It is possible to calculate the exothermicity of

of reaction (13) from thermochemical data.

$\Delta Hf\ (CF_3)$ = -119 K cals/mole [53,60,65]

$\Delta Hf\ (CF_3H)$ = -169 K cals/mole [108,65]

$\Delta Hf\ (HI)$ = 6 K cals/mole [115]

$\Delta Hf\ (I)$ = 25.5 K cals/mole [115]

Therefore, for the reaction

$$CF_3 + HI \longrightarrow CF_3H + I \qquad (13)$$

ΔH = -51 K.cals./mole. The reaction is therefore exothermic to the extent of 51 K cals/mole as compared with 18 K cals/mole. for the reaction

$$CF_3 + PhCH_3 \longrightarrow CF_3H + PhCH_2 \qquad (6)$$

The difference in exothermicities is the difference between $D(PhCH_2 - H)$ and $D(H - I)$ and it would be expected that the activation energy for reaction (13) would be less than for reaction (6). From the experimental data, no estimate of either activation energy can be made.

If we use the approximate Hirschfelder rule that the activation energy for the attack of a radical on a molecule is 5% of the bond which is broken, we have

E_6 = 5% of 84 = 4.2 K cals./mole.

and E_{13} = 5% of 71 = 3.55 K. cals./mole.

If the pre-exponential factors are the same for the two reactions, then, for equivalent concentrations we have that the ratio of rate constants at 800° K is

$$\frac{k_{13}}{k_6} = 10^{\frac{4,200 - 5,550}{4.57.800}} = 1.5$$

The experimentally found ratio of rate constants is much greater than 1.5 and this probably reflects the innaccuracies in the activation energies calculated by the Hirschfelder rules.

Since the results using the Hirschfelder rules were in such poor agreement with experimental data, an attempt was made to compare the work with some on $C H_3$ radicals. A fairly reliable estimate of the difference in activation energies for the reactions

$$C H_3 + I_2 \longrightarrow C H_3 I + I \qquad (4a)$$

$$C H_3 + H I \longrightarrow C H_4 + I \qquad (13a)$$

is available from the work of Ogg and Williams[114]. They found that $E_{13a} - E_{4a}$ was 750 cals/mole and that the ratio of the temperature independent factors for these reactions was $B_{13a}/B_{4a} = 0.25$.

If we assume that the constants for the reactions involving CF_3 radicals have the same values, and that the main competition for CF_3 radicals is between HI and I_2, the ratio of rate constants at 760°K would be

$$\frac{k_4}{k_{13}} = \frac{1}{.25} \cdot 10^{\frac{750}{4.57.760}} = 6.5$$

Thus, for only 1% of the CF_3 radicals to take part in reaction 4, we would require an HI : I_2 ratio of 650 : 1. All the back reaction appeared to be stopped when the HI : I_2 ratio was of the order of 70 : 1 (figure 27). This would indicate that the difference $E_{13} - E_4$ is less than 750 cals./mole or that the temperature independent

factors are different for the cases of CF_3 and CH_3 radicals.

The Reaction $I + CF_3I \longrightarrow CF_3 + I_2$

Much of the present investigation was carried out before it was realised that reaction (14) took place.

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

It is necessary to assess the extent of this reaction under various conditions before the results can be properly interpreted. In evaluating the rate constant $C_2 = k_{14}$ and the related C_2' for this reaction, it has been assumed that the equilibrium

$$I_2 \rightleftharpoons I + I$$

is established. Data by Rabinowitch and Wood[115] on the kinetics of recombination of iodine atoms can be used to calculate whether it is reasonable to use the equilibrium concentration of iodine atoms in the rate expression. Their results have been confirmed by more recent flash photolysis work. The data indicate that under all the conditions used in the flow system, the combination of iodine atoms will be mainly a heterogeneous reaction on the wall and that the limiting rate step will be the rate of diffusion to the wall. Atoms formed in the gas phase will undergo collisions in diffusing to the wall where in this case they will combine. This is discussed in detail by Semenoff[116] but for our purposes the formula given by Bursian and Sorokin[117] is sufficiently accurate. This states that the number of collisions n made by a particle in diffusing to the wall of a cylindrical vessel is given by

$$n = \frac{3}{32} \frac{d^2}{\lambda^2}$$

where d = diameter of cylindrical vessel in cms.

λ = mean free path of particle in cms.

The mean free path may be calculated from

$$\lambda = \frac{1}{\sqrt{2}\,\pi\,\sigma^2 m}$$

where σ = molecular diameter in cms.

m = no. of molecules / c.c.

For simplicity, it can be assumed that σ is about the same for all molecules = 5.8 Å.

Taking the most extreme case in the flow system of 0.6 mms. CF_3I and a total pressure of 7.6 mms, we have at 758°K

$$m = 10^{17} \text{ molecules / c.c.}$$

$$\sigma^2 = 14.4 \times 10^{-16} \text{ cms}^2$$

$$\lambda = 1.56 \times 10^{-3} \text{ cms}$$

If we ignore the thermocouple well and take the diameter of the reaction vessel as 2.5 cms.,

$$n = \frac{3}{32} \frac{d^2}{\lambda^2} = \frac{3}{32} \cdot \frac{6.25}{2.44.10^{-6}}$$

$$= \underline{2.4.10^5 \text{ collisions}}.$$

Thus in diffusing to the wall, an iodine atom would make $2.4.10^5$ collisions with all kinds of molecules, and

$$\frac{.6}{7.6} \times 2.4 \times 10^5 = 1.9 \times 10^4 \text{ collisions with } CF_3I \text{ molecules.}$$

If we assume that the steric factor for the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2$$

is one, and that the number of collisions in which reaction occurs is given by

No. of fruitful collisions = total no. of collisions x $e^{-E/RT}$

then the reaction occurs if the activation energy is less than 15 K cals./mole. It was found experimentally that the activation energy for this reaction was 18 K cals/mole., so that even in the worst case, if conditions are as bad as has been assumed and recombination of iodine atoms occurs only on the wall, an iodine atom will have an opportunity to form an iodine molecule before it attacks a CF_3I molecule. The equilibrium concentration of iodine atoms can therefore be used for calculations under flow conditions.

No work has been published on the efficiency of hydrogen iodide as a third body for the recombination of iodine atoms. The most inefficient gas which has been found for the homogeneous recombination of iodine atoms is helium, and even in this gas the combination is a homogeneous three body gas phase reaction at pressures above 500 mms. Hg. It would therefore be not unreasonable to assume that in the sealed tube reactions with an HI pressure of 600 mms. that the combination will also be a three body gas reaction. All four sets of workers[115,118,119,120] have found that the rate constant $\underline{k}$ for the combination of iodine atoms in the presence of helium at room temperature was about 10^{-32} (concentrations in molecules/c.c.) in the expression

$$\frac{-d(I)}{dt} = k\,(I)^2\,(He)$$

If we assume that the reaction has zero energy of activation, the

rate constant at the reaction temperature can be taken as being 10^{-32} even if HI is as inefficient as He in effecting the recombination of iodine atoms. In the fastest reaction studied in the static system, the mean rate of iodine atom formation was 1.5×10^{15} atoms c.c.$^{-1}$ sec.$^{-1}$. In a concentration of HI of 10^{19} molecules / c.c. a rate of recombination of I atoms of 1.5×10^{15} atoms c.c.$^{-1}$ sec.$^{-1}$ can be achieved with a concentration of I atoms given by

$$1.5.10^{15} = 10^{-32} (I)^2 (10^{19})$$

$$\therefore (I) = 1.14.10^{15} \text{ atoms / c.c.}$$

At 500°K this corresponds to 6.10^{-4} mms. of iodine which is about .01% decomposition of the smallest concentration of CF_3I used in the sealed tubes. Thus the rate of homogeneous combination of iodine atoms is so fast that once again the equilibrium

$$I_2 \rightleftharpoons I + I$$

is set up almost immediately and the equilibrium concentration of iodine atoms may be used in calculations.

The rate constants calculated for reaction (14)

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

can therefore be taken as correct. The relation of the rate constants obtained under flow conditions to those which would be expected from extrapolation of the data from the static system may now be examined.

The rate expression is

$$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2(I)(CF_3I)$$

or $$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2'(I_2)^{\frac{1}{2}}(CF_3I)$$

The relationship between C_2 and C_2' is $C_2' = C_2 K_c^{\frac{1}{2}}$

where K_c is the equilibrium constant in units of moles/l for the system

$$I_2 \rightleftharpoons I + I$$

Under flow conditions, it would be a very poor approximation to use

$$(I) = K_c^{\frac{1}{2}}(I_2)^{\frac{1}{2}}$$

so values of C_2' at the temperatures of the flow experiments would be inaccurate. The values of C_2' from the sealed tube experiments have therefore been corrected to values of C_2 and are listed, together with the flow results in table 36.

TABLE 36 Variation of C_2 with Temperature.

	T (°K)	$\frac{1}{T} \times 10^3$	C_2' $l^{\frac{1}{2}}moles.^{-\frac{1}{2}}sec.^{-1}$	C_2 $l.moles.^{-1}sec.^{-1}$	log C_2
Flow Expts.	758	1.319		$8.65.10^5$	5.937
	698	1.455		$2.55.10^5$	5.367
	488	2.049	$5.20.10^{-4}$	1,010	3.005
			to $6.52.10^{-4}$	to 1,220	to 3.085
Static Expts.	466	2.146	$9.26.10^{-5}$	424	2.627
	453	2.208	$4.06.10^{-5}$	324	2.510
	449	2.227	$2.72.10^{-5}$	260	2.415
	440	2.275	$1.32.10^{-5}$	189	2.276
	440	2.275	$9.44.10^{-6}$	135	2.130

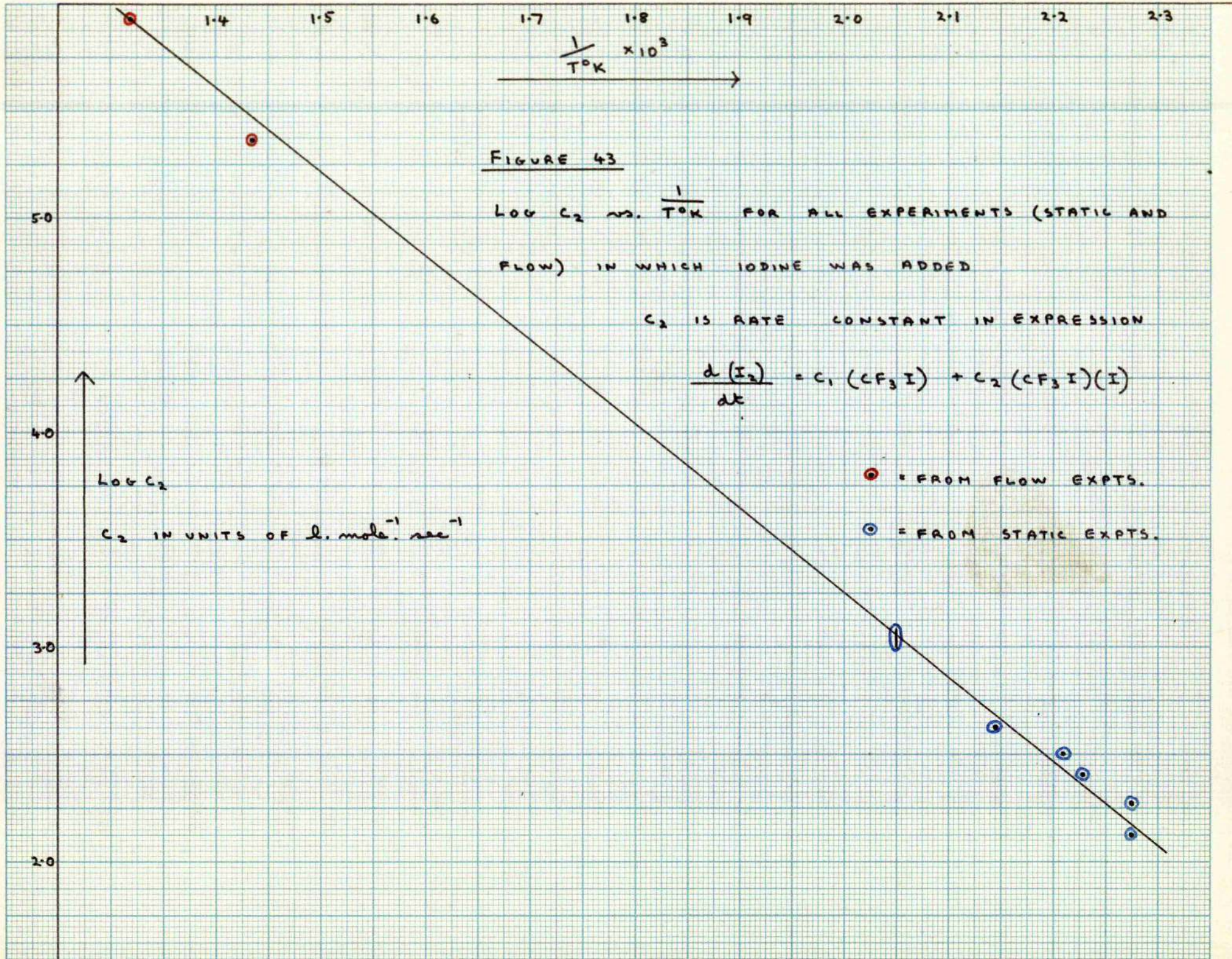


FIGURE 43

LOG C_2 vs. $\frac{1}{T°K}$ FOR ALL EXPERIMENTS (STATIC AND FLOW) IN WHICH IODINE WAS ADDED

C_2 IS RATE CONSTANT IN EXPRESSION

$$\frac{d(I_2)}{dt} = C_1 (CF_3I) + C_2 (CF_3I)(I)$$

◉ = FROM FLOW EXPTS.

⊙ = FROM STATIC EXPTS.

In figure 45, log C_2 is plotted against $\frac{1}{T}$. More weight has been given to the point at 758°K which was the result of several experiments than to the point at 698°K which was derived from one experiment only. The slope of the line gives E = 17.6 K.cals./mole for the reaction

$$I + CF_5I \longrightarrow CF_5 + I_2 \qquad (14)$$

Considering the difficulty of knowing the reaction volume accurately in the flow system and the approximate way in which the values of C_2 were calculated for the flow experiments, this value is in good agreement with the value of E = 18.2 K cals./mole obtained from only the static experiments in which iodine was added. (Figure 42). Extrapolation of this data has been used in the discussion of the results of the experiments with toluene.

The temperature independent factor B in the Arrhenius equation

$$C_2 = Be^{-E/RT}$$

is $10^{10.8}$. This is a not unreasonable value for the collision frequency of I and CF_5I and would suggest that the steric factor for the reaction is about unity. The effect of the extent of this reaction on the interpretation of the other data may now be considered.

The Variation of CF_5I Pressure in the Flow System.

The results obtained in these experiments showed that the rate of production of iodine was second order in CF_5I, and this was at the time interpreted as being due to the concentration of activated molecules not being maintained at the equilibrium value at low pressures.

Allowance can be made for the extent of the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

by the rather approximate method used to calculate the rate constants under flow conditions. No iodine was added in these experiments so the initial iodine atom concentration is zero. The iodine atom concentration at the furnace exit may be found from the iodine produced and the extent of dissociation of the iodine. As an approximation, half of this value may be taken as the effective mean iodine atom concentration. The mean CF_3I concentration may be evaluated, and, using the experimentally derived value of C_2 at $758^{\circ}K = 8.65.10^5$ $l.moles^{-1}sec^{-1}$ it is possible to calculate the rate of formation of iodine due to reaction (14). The results are presented in table 37, average values for the experiments being quoted.

TABLE 37 Extent of Iodine Catalysis in Experiments on Variation of CF_3I Pressure at 758°K

Expt No.	Pressure CF_3I (mms.Hg)	Contact Time (secs)	Total Percent Decomp	Mean (I)x10^8 gm.atoms/l.	Mean CF_3Ix10^6 moles/l.	$\frac{d(I_2)}{dt}$ x10^8 catalytic moles.l^{-1} sec^{-1}
78	.076	.545	3.57	2.96	1.575	4.05
76	.138	.545	5.1	5.20	2.68	12.05
64	.256	.559	7.0	8.84	4.31	32.9
68	.241	.526	7.4	9.25	4.39	35.1
65	.254	.581	8.0	9.89	5.15	44.0
75	.521	.570	9.5	12.7	6.46	71.0
74	.479	.572	15.0	18.6	9.5	152.5
77	.581	.554	14.0	21.2	11.4	209

Table 37 Con.

Expt No	In 10 mins. Moles I_2 x 10^6 catalytic	Total Moles I_2 x 10^6	Moles I_2 x 10^6 by initial split	Moles CF_3I x 10^4 injected	%Decomp due to initial split	% Decomp corrected to 0.55 secs.
78	4.87	13.5	8.6	3.77	2.28	2.30
76	15.5	33.0	17.5	6.35	2.76	2.79
64	42.0	80	38	11.45	3.32	3.26
68	45.6	94	48	12.50	3.84	4.00
65	56.6	97	40	12.14	3.30	3.14
75	91.0	145	54	15.3	3.52	3.40
74	195	283	88	22.0	4.00	3.84
77	268	365	97	26.1	3.72	3.68

FIGURE 44

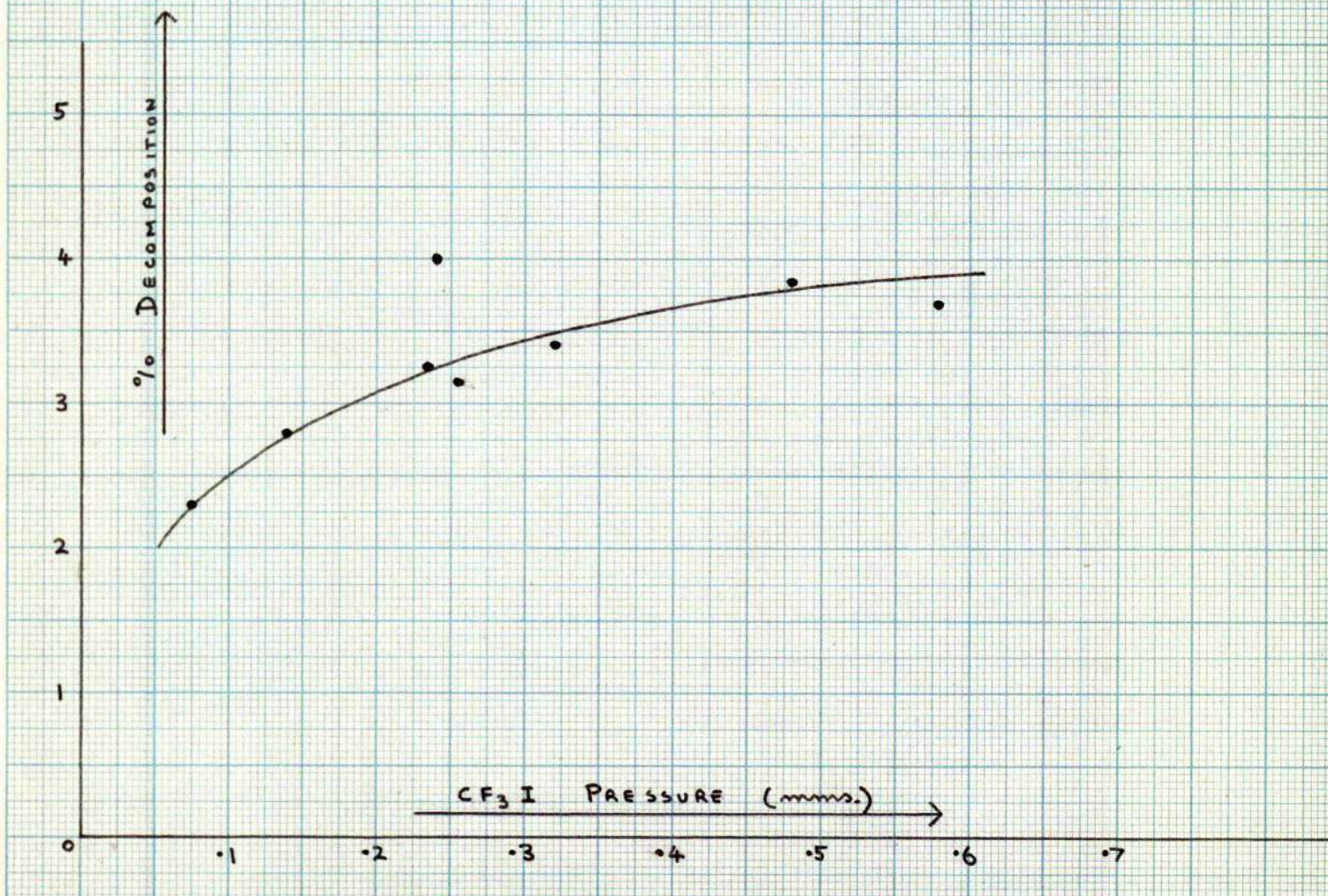
PERCENTAGE DECOMPOSITION OF CF_3I IN 0.550 secs.

DUE TO INITIAL SPLIT vs. CF_3I PRESSURE

758°K

HI PRESSURE = 1.97 to 2.33 mms.

N_2 PRESSURE = 4.07 to 4.66 mms.



Ten minutes was selected as a convenient time in the above calculations since many of the experiments had been conducted for this period.

In figure 44 is plotted the pressure of CF_3I against the percentage decomposition corrected to 0.55 secs due to reaction (1)

$$C F_3 \longrightarrow C F_3 + I \qquad (1)$$

It is seen that the rate of this reaction step is not first order in CF_3I but that it is not nearly so dependent on CF_3I concentration as is the total rate (cf.figure 28). The fall off in rate in figure 44 is probably genuinely due to the Hinshelwood-Lindemann effect. However, at 0.10 mms. CF_3I, the rate of initial split of CF_3I is not second order. It would therefore be impossible to derive a value for the efficiency of an inert gas by experiments at this pressure of CF_3I and use of the method employed earlier. The derived values of $\alpha_{A'}$ α_{N_2} and $\alpha_{C_6H_5CF_3}$ have therefore no meaning as efficiencies and the low values obtained can be explained from the above calculations. It is interesting that the reciprocal of the assumed first order rate constant for the overall reaction when plotted against the "effective pressure" gave a straight line (figure 51) when the results were not due to the effect then suspected.

However, for the rate of initial split of CF_3I, a plot of $\frac{1}{C_1}$ against $\frac{1}{[CF_3I]}$ should give a straight line where C_1 is the constant in the rate expression

$$\frac{d\,(I_2)}{dt} = C_1(CF_3I) + C_2(CF_3I)(I)$$

FIGURE 45

$\frac{1}{C_1}$ vs $\frac{1}{(CF_3I)}$ AT 758°K

C_1 IS ASSUMED FIRST ORDER RATE CONSTANT IN EXPRESSION $\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2(CF_3I)(I)$

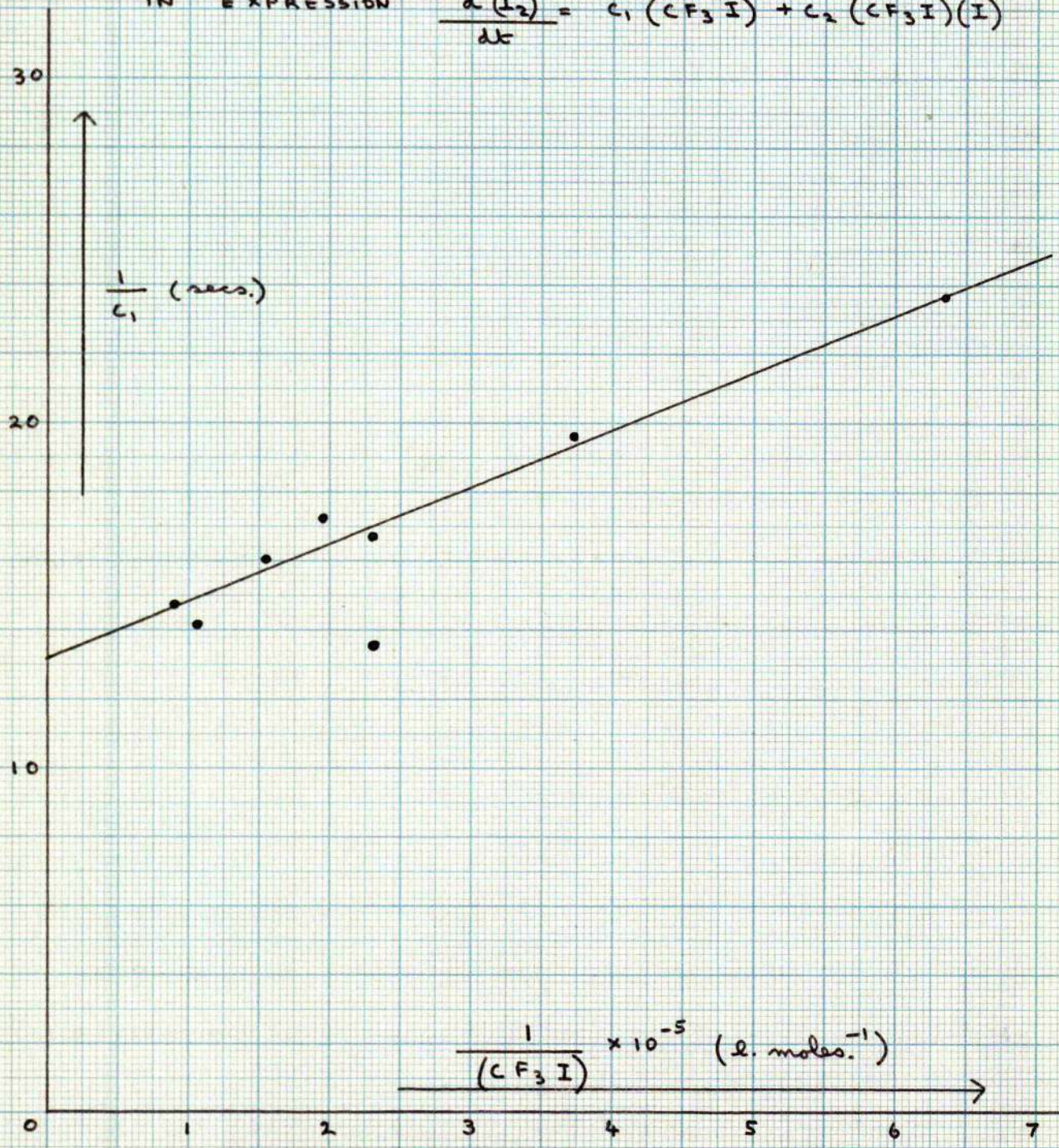


Table 38 contains the necessary data and figure 45 is a plot of $\frac{1}{C_1}$ against $\frac{1}{CF_3I}$

TABLE 38 Variation of C_1 with CF_3I Concentration.

Expt. No.	% Decomp. due to initial split	Contact Time (secs)	C_1 ($secs^{-1}$)	$\frac{1}{C_1}$ (secs)	$\frac{1}{CF_3I} \times 10^{-5}$ $l.moles^{-1}$
78	2.28	.545	4.22×10^{-2}	25.7	6.55
76	2.76	.545	5.11×10^{-2}	19.6	3.73
64	3.32	.559	6.01×10^{-2}	16.7	2.32
68	3.84	.526	7.44×10^{-2}	13.5	2.28
65	3.30	.581	5.79×10^{-2}	17.2	1.94
75	3.52	.570	6.26×10^{-2}	16.0	1.55
74	4.00	.572	7.11×10^{-2}	14.05	1.05
77	3.72	.554	6.81×10^{-2}	14.7	.88

It is seen that the graph in figure 45 is a reasonably straight line despite the fact that no allowance has been made for other gases. However, since the reaction was being investigated in a region where second order behaviour was not accurately obeyed, the low pressures of inert gases present probably have little effect. From figure 45,

C_1 at ∞ pressure = $7.58.10^{-2}$ $secs.^{-1}$

C_1 at 0.10 mms. CF_3I = $4.76.10^{-2}$ $secs.^{-1}$

At 0.10 mms CF_3I, therefore, the rate is 0.65 of the true first order rate. It should be a reasonable approximation to treat the initial split as being effectively first order at all pressures used.

Variation of Contact Time in the Flow System.

At the time these experiments were performed, it was thought that the results might be due to a systematic error in the flow system. Moore[85] performed calculations which indicated that there should be no appreciable systematic error in contact time at the flow rates used here, but, nevertheless, Lapage[103] and Cundall[3] both obtained results which suggested that the effective contact time was less than the calculated contact time at fast flow rates with this type of apparatus. In our case, most of the effect must be due to the autocatalytic nature of the reaction. Because of the possible errors in the values of the contact time, no quantitative deductions have been made from the results obtained.

Temperature Coefficient and Variation of Surface Area.

When the temperature was varied at three different surface areas, the results were interpreted in terms of second order rate constants and these were used to derive an activation energy. In the light of present knowledge about the reaction, this original interpretation was wrong and the activation energies and temperature independent factors obtained have no simple meaning. It is possible to calculate approximately the extent of the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

at different temperatures by using values of C_2 derived from figure 45 and treating the data in the same manner as the results on the variation of CF_3I pressure (table 37). The percentage decomposition

due to the initial split may then be evaluated and the assumed first order rate constants, C_1 , for reaction (1) derived.

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

The results for each end of the temperature range at the three values of $\frac{S}{V}$ are presented in table 59.

TABLE 59 Values of C_1 at 758°K and 712°K

Expt. No.	$\frac{S}{V}$ (cms^{-1})	Total % Dec.	% Dec due to initial split	C_1 first order ($secs^{-1}$)	log C_1	T (°K)	$\frac{1}{T} \times 10^3$
93	1.95	3.59	1.35	1.80×10^{-2}	$\bar{2}.256$	758	1.319
94	3.96	6.27	3.31	4.34×10^{-2}	$\bar{2}.637$	758	1.319
95	6.15	7.9	3.96	5.57×10^{-2}	$\bar{2}.746$	758	1.319
101	1.95	.345	.172	2.26×10^{-3}	$\bar{3}.354$	712	1.404
100	3.96	.63	.372	4.57×10^{-3}	$\bar{3}.660$	712	1.404
104	6.15	.80	.504	6.34×10^{-3}	$\bar{3}.802$	712	1.404

The results in table 59 show that even at the smallest decompositions used, there is still an appreciable amount of catalysis by iodine. It is possible to calculate the percentage decomposition due to the initial split for each experiment performed and hence to derive a value of C_1. The approximate method of calculation and the fact that the initial split was not first order in CF_3I made this rather pointless, and the results from each end of the temperature range have been used to derive approximate orders of magnitude for the constants in the equation for the temperature

dependence of C_1.

From the above data values of A and E in the Arrhenius Equation $C_1 = A \exp\left(\frac{-E}{RT}\right)$ have been calculated for each value of $\frac{S}{V}$. The values derived are:-

$\frac{S}{V}$ (cms^{-1})	log A	E (K cals/mole)
1.95	12.6	49.5
3.96	13.7	52.5
6.15	13.4	51.0

Considering the crude method of evaluating C_1, the values of E remain fairly independent of surface to volume ratio and the values of A are of a reasonable magnitude for first a first order reaction. Nevertheless, the rate of initial split does increase with the $\frac{S}{V}$ ratio. The results on the rate of initial split are in this respect similar to the results obtained on measurements of the overall rate (figure 33) and may be interpreted in the same way as showing that the mechanism remains independent of $\frac{S}{V}$.

In making the above calculations, it was tacitly assumed that the rate of reaction (14)

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

remained independent of surface to volume ratio. This is a reasonable assumption for it was found that the rate of reaction was independent of surface area in the sealed tube reactions where it will be shown that reaction (14) predominates.

It would not readily be possible to explain the results by assuming that the initial split of CF_3I took place completely on the wall. The dependence of the rate on CF_3I pressure to an order greater than one does not agree with the laws of adsorption of gases. Also, if CF_3 radicals were formed on a glass wall, it would be expected that SiF_4 would be produced in amounts sufficiently large to be detected.

It might seem possible to account for the results by proposing that the initial step was a bimolecular reaction between HI and CF_3I on the wall. In this case, the independence of the rate on HI pressure could be explained by assuming that the wall was saturated with HI molecules above a certain pressure. However, the occurrence of the CF_3I concentration to an order greater than one is once again difficult to explain. There is also a considerable amount of evidence which shows the presence of free CF_3 radicals and this wall reaction theory contradicts this.

The effect of increase in surface area would be to increase the rate of heterogeneous recombination of I atoms and this would, if anything, decrease the rate of iodine production.

It might be suggested that the surface was a very efficient agent in transferring energy to CF_3I molecules and that this increased the rate of initial split. This seems to be a possible explanation of the phenomenon but it is rather unsatisfactory since the rate already appeared to be so near first order.

The values found for the activation energy of reaction (1) should be identifiable with $D(CF_3-I)$. A value of $D(CF_3-I)$ of 51 ± 2 K cals/mole. would appear to be not unreasonable and the "normal" values of the A factors in the Arrhenius equations support this interpretation of the results. However, owing to the crude method used to derive values of the rate constants and the fact that the reaction was not truly first order, the results can only be regarded as very approximate.

The Reactions in Sealed Tubes.

In an attempt to find out how much of the iodine production in these experiments was due to the iodine catalysed reaction, approximate calculations similar to the type performed for the flow experiments were carried out. The average $(I_2)^{\frac{1}{2}}$ in units of $(\text{moles/l})^{\frac{1}{2}}$ and the average CF_3I concentration may be evaluated from the experimental results. Values of C_2 and hence of C_2' for the rate of reaction (14)

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

may be found from figure 43. It is then possible to calculate the rate of formation of iodine due to the iodine catalysed reaction and to compare this with the total rate of formation of iodine. Such calculations have been performed for the series of experiments where the concentration of CF_3I was varied, for the series where the temperature was altered and for the series with differing reaction times. The results are listed in table 40.

TABLE 40 Extent of Catalysis by Iodine in Sealed Tube Reactions.

Expt No.	Tempr °K	Mean $CF_3I \times 10^4$ moles/l	Mean $\sqrt{I_2} \times 10^5$ $(moles/l)^{\frac{1}{2}}$	$C_2' \times 10^5$ $l^{\frac{1}{2}} moles^{-\frac{1}{2}} sec^{-1}$	Reaction Time (secs)	Moles $I_2 \times 10^6$ catalytic	Moles $I_2 \times 10^6$ found
S16	522	1.155	2.52	7.08	10,800	14.1	14.9
S15	522	2.21	3.98	7.08	10,800	45.7	41.3
S17	522	4.18	6.74	7.08	10,800	150	122
S18	522	4.91	7.86	7.08	10,800	212	169
S28	522	5.00	7.86	7.08	10,800	215	169
S29	522	1.085	2.14	7.08	10,800	12.5	12.5
S19	505.5	5.93	3.68	2.24	10,800	56.8	57.0
S21	499.5	6.1	2.43	1.59	10,800	17.9	16.1
S22	515.5	5.55	5.50	5.98	10,800	91.5	85
S30	499.5	5.71	5.00	1.59	29,580	94	69.5
S34	499.5	5.26	6.95	1.59	42,500	175	135

Table 40 shows that the calculated rate of iodine production due to reaction (14)

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

is in almost all cases greater than the total rate actually found and in many cases is within 10% of the experimental result.

The considerable discrepancies between theoretical calculation and experimental result in experiments S18, S28, S30 and S34 may be due to the arithmetic mean concentrations being very poor approximations to the effective mean values over such large percentage

decompositions.

From the above calculations, it would appear that almost all the iodine production in the sealed tube reactions under the conditions examined can be attributed to the processes

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

$$\text{and } CF_3 + HI \longrightarrow CF_3H + I \qquad (15)$$

This means that in the expression for the rate of formation of iodine

$$\frac{d(I_2)}{dt} = C_1(CF_3I) + C_2(CF_3I)(I)$$

$$\text{or } \frac{d(I_2)}{dt} = C_1(CF_3I) + C_2'(CF_3I)(I_2)^{\frac{1}{2}}$$

the term $C_1(CF_3I)$ may be neglected. Under these conditions, C_2' and hence C_2 may be evaluated by means of the integrated expression

$$C_2' = \frac{2.303}{t\sqrt{a}} \log \frac{\sqrt{a} + \sqrt{x}\ \text{final}}{\sqrt{a} - \sqrt{x}\ \text{final}}$$

The values of C_2' and of C_2 for the above experiments are listed in table 41.

TABLE 41 Values of C_2' and C_2 from Static Experiments without added Iodine.

Expt. No.	Tempr. (°K)	$\frac{1}{T} \times 10^3$	$C_2' \times 10^5$ $l^{\frac{1}{2}}moles^{-\frac{1}{2}}sec^{-1}$	C_2 $l.moles^{-1}sec^{-1}$	log C_2
S16	522	1.916	7.38	4,150	3.618
S15	522	1.916	6.35	3,570	3.553
S17	522	1.916	5.55	3,120	3.494
S18	522	1.916	5.50	3,090	3.490
S28	522	1.916	5.40	3,030	3.482
S29	522	1.916	7.05	3,860	3.587
S19	505.5	1.978	2.26	2,310	3.364
S21	499.5	2.002	1.45	1,824	3.261
S22	515.5	1.951	3.60	2,790	3.446
S30	499.5	2.002	1.17	1,470	3.168
S34	499.5	2.002	1.20	1,510	3.179

At 522°K, there is considerable variation in the values of C_2. These were the experiments in which the effect of variation of CF_3I pressure was studied. The values of C_2 are probably low at the higher concentrations of CF_3I (experiments S17, S18, S28) where some back reaction may have taken place; a small amount of C_2F_6 was found in experiment S28.

In the experiments at 499.5°K where the effect of variation of reaction time was studied, it is seen that C_2 for experiment S21 is about 20% higher than the values of C_2 for experiments S30 and S34.

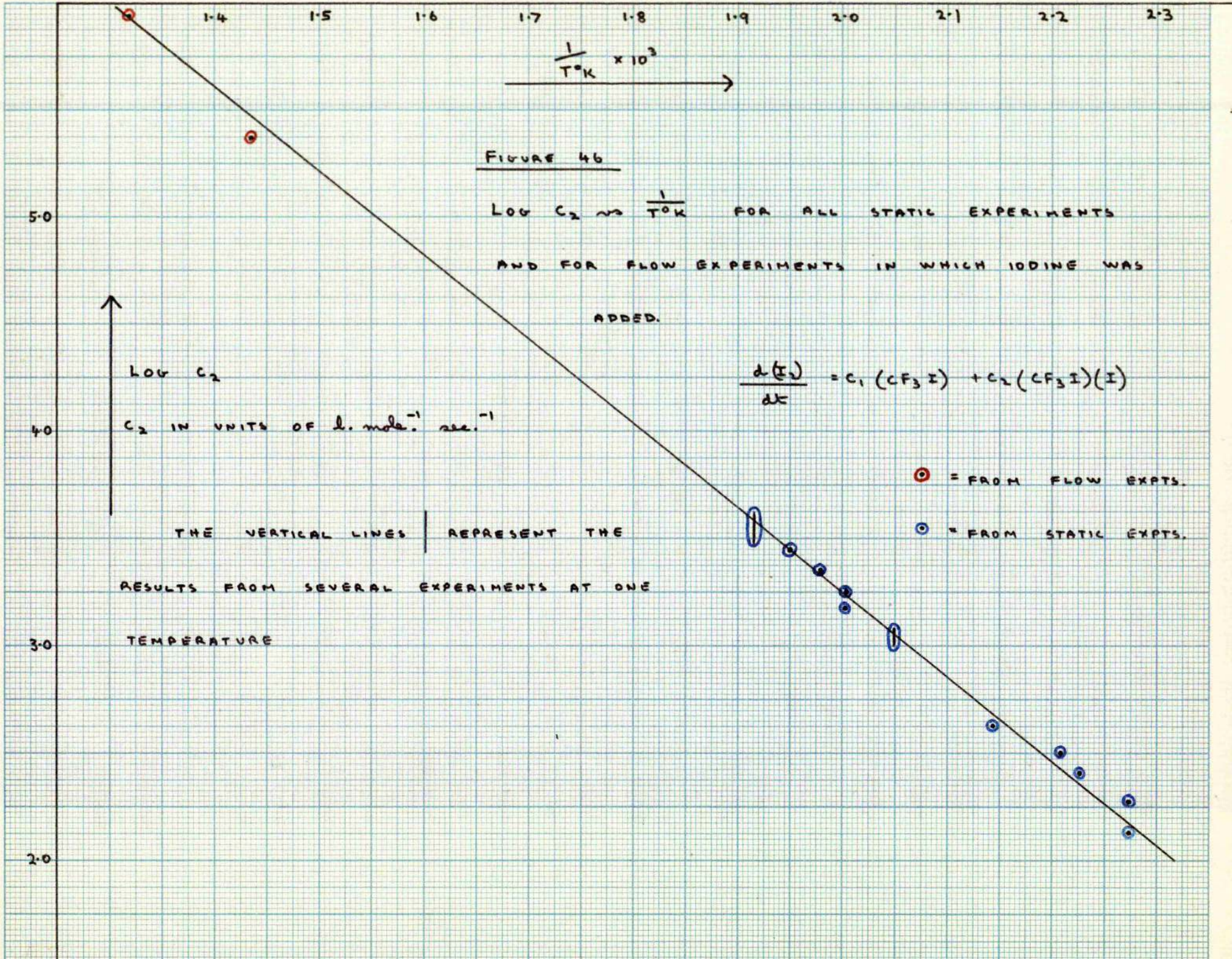


FIGURE 46

LOG C_2 vs $\frac{1}{T°K}$ FOR ALL STATIC EXPERIMENTS AND FOR FLOW EXPERIMENTS IN WHICH IODINE WAS ADDED.

This would suggest that the results for experiment S21 are in error; any conclusions drawn from figure 39 would therefore tend to contradict the theory which has been put forward.

These values of log C_2 have been plotted against $\frac{1}{T}$ in figure 46 together with the data which has already been presented in table 56 and figure 45. A reasonably straight line is obtained in figure 46 over the very large temperature range 440°K to 758°K. The values of B and E in the Arrhenius equation

$$C_2 = B \exp\left(\frac{-E}{RT}\right)$$

are $B = 10^{10.8}$ l.mole^{-1}sec^{-1} and $E = 17.6$ K cals./mole.

It was thought that a better line might be drawn through the points from the experiments in sealed tubes only. There is the difficulty when trying to correlate data from flow and static systems that the reaction volume may not have been known accurately in the flow system and therefore the results may not be directly comparable. There is the additional trouble that in the present work the values of C_2 for the flow system were calculated by a rather approximate method. The data from the static system alone are over a range of 82 C° and should therefore give reasonably accurate results. The results are plotted in figure 47. This plot gives that E = 18.0 K cals/mole and that $B = 10^{11.1}$ l.mole^{-1}sec^{-1}.

In figures 42, 43, 46 and 47 values of E from 17.6 to 18.2 K cals/mole and values of B from $10^{10.8}$ to $10^{11.2}$ have been obtained. This would suggest that the activation energy for reaction (14)

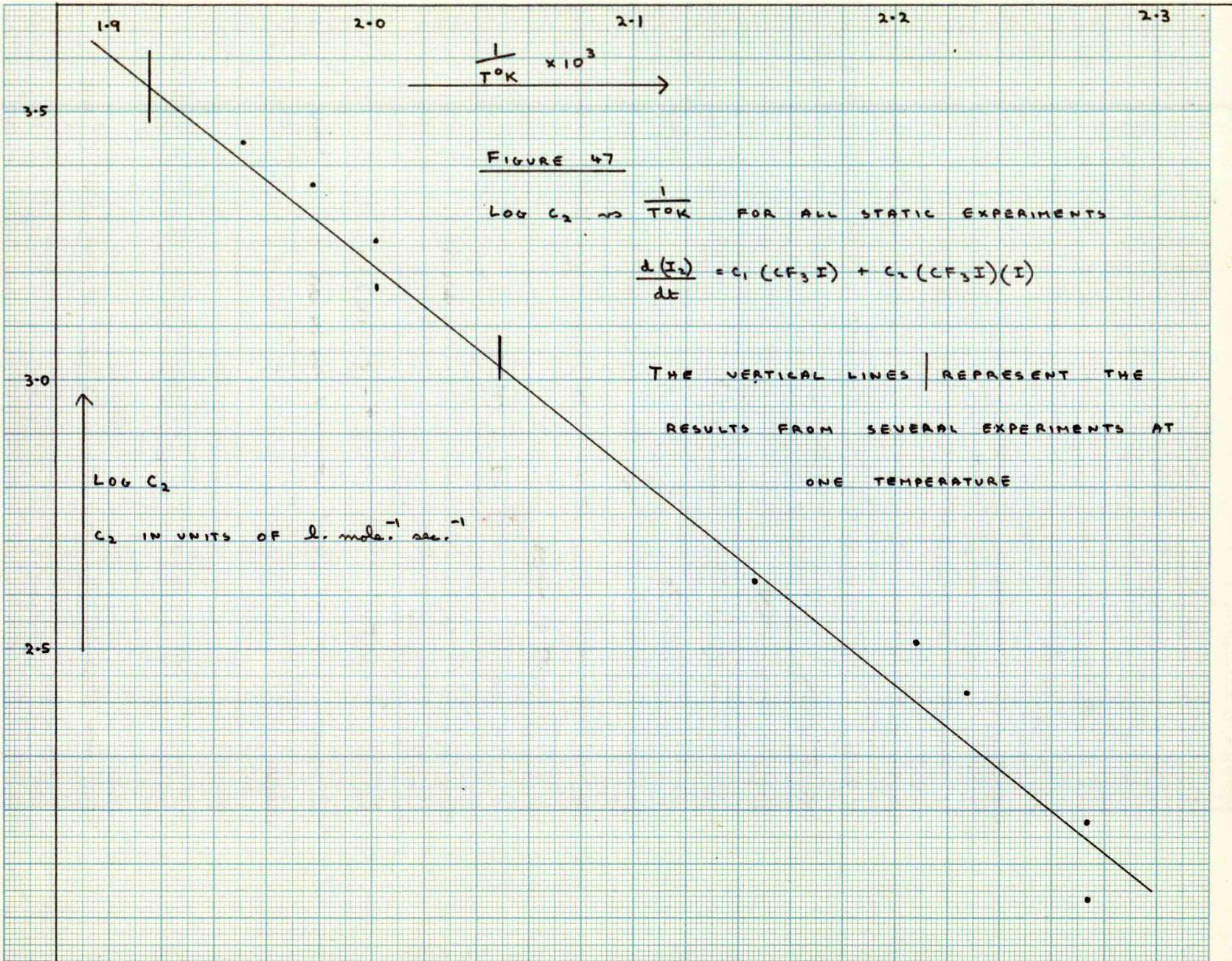


FIGURE 47

LOG C_2 vs $\frac{1}{T°K}$ FOR ALL STATIC EXPERIMENTS

$$\frac{d(I_2)}{dt} = C_1 (CF_3I) + C_2 (CF_3I)(I)$$

THE VERTICAL LINES | REPRESENT THE RESULTS FROM SEVERAL EXPERIMENTS AT ONE TEMPERATURE

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

lies within the range 18.0 ± 1 K cals/mole and that the steric factor for the reaction is about unity.

The CF_3-I Bond Dissociation Energy.

From the temperature coefficient data in the flow system, an approximate value of $D(CF_3\text{-}I) = 51 \pm 2$ K cals/mole was obtained. It is also possible to derive a value from other data obtained in this investigation.

Consider the reactions

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (4)$$

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

The data on the temperature dependence of the rate of reaction (14) gave an activation energy for this reaction of $E_{14} = 18.0 \pm 1$ K cals/mole. $D(CF_3\text{-}I)$ is therefore given by

$$D(CF_3\text{-}I) = 18.0 \pm 1 + D(I\text{-}I) - E_4$$

where D(I-I) is the bond energy in the iodine molecule.

At 470°, $D(I - I) = 56.4$ K.cals/mole.

Therefore, at 470°K, $D(CF_3I) = 54.4 \pm 1$ K cals/mole - E_4.

The value of $D(CF_3\text{-}I) = 51 \pm 2$ K.cals/mole is not of sufficient accuracy to justify deriving a value of $E_4 = 3.4 \pm 3$ K.cals./mole from the results.

Dacey[49] has suggested that the activation energy of the reaction

$$CF_3 + I_2 \longrightarrow CF_3I + I$$

is of the order of 1 K.cals./mole. In this investigation, it was

found that the back reaction occurred very readily which would again suggest a low activation energy for this reaction.

The reactions of methyl radicals with iodine have been studied by several workers and their findings are of interest since it would be expected that the activation energies would be very similar for the two reactions

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (4)$$

and $$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (4a)$$

In his investigation on the thermal reaction of methyl iodide with hydrogen iodide Ogg[38] concluded that reaction (4a) was a step in the mechanism. Jones[121] found that reaction (4a) was also a step in the decomposition of acetyl iodide and from Ogg's results estimated that E_{4a} was 12 K.cals./mole. Steacie[8] regards this as impossibly high.

It has been found[122] that methyl radicals react readily with iodine vapour in the temperature range 215° to 306° which would indicate a low activation energy for reaction (4a). Iodine has been used to "catch" methyl radicals[123] in a manner rather similar to that in which HI and toluene were used in this investigation. This again shows that reaction (4a) must have a low energy of activation.

Andersen and Kistiakowsky[124] obtain a value of $E_{4a} = 0.5 \pm 0.5$ K cals./mole by what Steacie[8] regards as "a rather dubious process of reasoning by analogy". The method used is as follows:-

E = 9 K cals/mole for $CH_3 + H_2 \longrightarrow CH_4 + H$

$E = 8$ K cals/mole for $H + H_2 \longrightarrow H_2 + H$

i.e. the difference in activation energies is about 1 K cal./mole.

Since $E = 0$ for the reaction $H + I_2 \longrightarrow HI + I$

$E = 0.5 \pm 0.5$ K cals/mole for $CH_3 + I_2 \longrightarrow CH_3I + I$

It would seem, therefore, that the activation energy for reaction (4)

$$CF_3 + I_2 \longrightarrow CF_3I + I$$

should lie within the range 1 ± 1 K cals/mole.

This would give a value of $D(CF_3\text{-}I) = 53.5 \pm 2$ K cals/mole at $500^\circ K$.

It was not considered that this value was of sufficient accuracy to justify correction to $0^\circ K$. The value of $D(CF_3\text{-}I) = 55.5 \pm 2$ K cals/mole agrees with the lower limit of error of the value proposed by Farmer et alia[60] of 57 ± 4 K cals/mole and with the upper limit of the value obtained by Dibeler, Reese and Mohler[78] of 48.5 ± 5 K.cals./mole. The value of 45.7 K. cals/mole obtained by Marriott and Craggs[79] would seem to be definitely too low.

The value of $D(CH_3\text{-}I)$ is fairly well established as about 54 K. cals/mole[5, 125]. Thus there would appear to be little difference between $D(CF_3\text{-}I)$ and $D(CH_3\text{-}I)$. This is in agreement with the results found for CF_3Br and CH_3Br, and for CF_3Cl and CH_3Cl.

These results may be summarised:-

Bond Energy (K cals./mole)	Reference	Bond Energy (K cals/mole)	Reference
D (CF_3-Cl) = 79.5	53	D(CH_3-Cl) = 81.2	54
D (CF_3-Cl) = 83	60		
D (CF_3-Br) = 64.5	51	D(CH_3-Br) = 67	126
D (CF_3-I) = 55.5 ± 2		D(CH_3-I) = 54	3,125

At 758°K, it was found that for reaction (1)

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

k_1 was $7.58.10^{-2}$ $secs^{-1}$ when the rate was first order (figure 45). If it is assumed that at 758°K the activation energy of reaction (1) is 55.5 K cals/mole., the temperature dependence of k_1 is given by

$$k_1 = 10^{14.5} \exp\left(\frac{-55,500}{RT}\right) secs^{-1}$$

This value for the temperature independent factor of $10^{14.5}$ is about the upper limit of the "normal" size and gives support to the proposed mechanism. This expression has been used to calculate the value of k_1 at 797°K for the interpretation of the data obtained in the presence of toluene.

Comparison with the Pyrolysis of Methyl Iodide.

From the investigations on the pyrolysis of methyl iodide, it was found that D(CH_3-I) = 54.7 K cals/mole. This is very similar to the values found here for D(CF_3-I). In each case, the initial step is a split into a radical and an iodine atom. However, the other features of the decompositions would appear to be dissimilar. No back reaction

was found with methyl iodide at pressures of up to 1 mm. CH_3I and even under the high pressure conditions used, the back reaction was completely stopped by toluene. There was considerable back reaction even at low pressures in the case of CF_3I, toluene would not react with all the CF_3 radicals but hydrogen iodide proved efficient in stopping the back reaction. No CF_4 was found whereas CH_4 was the main hydrocarbon product from the pyrolysis of CH_3I. The decomposition of CH_3I was second order in iodide pressure at 0.1 mms. methyl iodide while the rate of initial split of CF_3I was almost first order at these pressures. The reaction

$$I + CH_3I \longrightarrow CH_3 + I_2$$

was not found. It had been calculated[5] that this reaction would not occur if the steric factor was of the order of 10^{-2} or less. In the case of CF_3I, the reaction

$$I + CF_3I \longrightarrow CF_3 + I_2$$

has been found to occur under all conditions examined and the steric factor was found to be about 1.

It is strange that the mechanisms should be so different and it would, as mentioned earlier, be interesting to examine the thermal decomposition of CH_3I - HI mixtures.

The pyrolysis of benzyl iodide has very recently been studied in St. Andrews by Gow and Horrex[29] using apparatus and techniques very similar to those employed here. The decomposition of benzyl iodide alone has been studied much more extensively and thoroughly than the

decomposition of CF_3I alone. Benzyl iodide decomposes according to the scheme

$$RI \rightleftharpoons R + I$$

$$R + I_2 \rightleftharpoons RI + I$$

$$I + I \rightleftharpoons I_2$$

$$R + R \longrightarrow R_2$$

where R = benzyl. The dimerisation of benzyl radicals is the rate determining step. It is suspected that the decomposition of CF_3I follows the above scheme where R = CF_3, but the data are not sufficiently extensive to prove this.

In the case of both iodides, sufficient HI appears to capture the radicals and identical kinetics are found in the presence of HI. Since these two iodides have such widely differing carbon iodine bond energies, and yet similar kinetics are obtained in the presence of HI, it would seem reasonable to expect other iodides in which the initial decomposition step was a split into a radical and an iodine atom to behave similarly in the presence of HI. If this was the case, the method would be of general use for determining values of D(C-I).

SUMMARY

The pyrolysis of trifluoromethyl iodide has been investigated under two entirely different sets of conditions

(i) in a low pressure flow system.

(ii) in sealed tubes at higher pressure.

In the flow system, nickel and pyrex reaction vessels were used. The nickel vessel was used when no material was added to react with CF_3 radicals which it was feared would attack pyrex glass. During the course of the investigation, it was decided to add toluene, hydrogen iodide and iodine as additional reagents. The conditions in the flow system were varied within the following limits:-

Temperature 698°K to 797°K

Contact Time .526 to 2.52 secs.

CF_3I Pressure 0.016 mms. to 0.58 mms.

Toluene Pressure 0 to 3.76 mms.

Hydrogen Iodide Pressure 0 to 4.08 mms.

N_2 carrier gas Pressure 1.50 to 14.5 mms.

A carrier gas Pressure 1.59 to 12.4 mms.

$C_6H_5CF_3$ Pressure 0 to 2.65 mms.

Pressure of added iodine (as atoms) 0 to .0176 mms.

Surface to Volume Ratio 1.95 to 6.15 cms^{-1}

Only pyrex reaction vessels were used in the sealed tube reactions. CF_3I was never heated alone but always in the presence of HI In

these reactions, conditions were varied within the limits:-

Temperature 440°K to 522°K

Reaction Time 10,800 secs. to 259,200 secs.

CF_3I Pressure 4.0 mms. to 37 mms.

Hydrogen Iodide Pressure 5.7 mms. to 565 mms.

Pressure of added iodine (as molecules) 0 to 5.0 mms.

An attempt was made to find the stoichiometry of the reaction under all conditions. In order to do this, titration, low temperature distillation, U.V. and I.R. absorption spectrophotometry and mass spectrometry were used. A reaction scheme has been proposed which agrees with the major experimental findings.

CONCLUSIONS.

1) The only initial step under all conditions examined was a split of CF_3I into a CF_3 radical and an iodine atom; the reaction is completely free radical.

2) When no other material is present to react with CF_3 radicals, the products are essentially C_2F_6 and iodine. There is a back reaction between CF_3 radicals and iodine which causes the rate of decomposition to fall off as the reaction proceeds. This is due to there being more iodine at the higher percentage decompositions to react with the CF_3 radicals and reform CF_3I. The reaction steps occurring are:-

$$CF_3I \rightleftharpoons CF_3 + I$$

$$CF_3I + I \rightleftharpoons CF_3 + I_2$$

$$I + I \rightleftharpoons I_2$$

$$CF_3 + CF_3 \longrightarrow C_2F_6$$

It is probable that the dimerisation of CF_3 radicals to form C_2F_6 may be the rate determining step under these conditions.

3) Addition of toluene showed the presence of CF_3 radicals and stopped the back reaction to some extent; the formation of C_2F_6 was suppressed, CF_3H was formed and the percentage decomposition was raised. All the CF_3 radicals could not be accounted for and the iodine containing products were complex, benzyl iodide and hydrogen iodide being produced as well as iodine. There was a small inert gas effect but few quantitative deductions can be made from the experiments with toluene.

4) Hydrogen iodide reacted much more readily with CF_3 radicals than did toluene. It was possible to obtain conditions in both flow and static systems where the rate of iodine production was independent of HI pressure. In these circumstances, all the CF_3 radicals appeared to react with HI and the only products seemed to be CF_3H and I_2 in the ratio 1:1.

5) It was found that reaction (14) occurred under all conditions studied

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

Because of this, the total rate of decomposition in the presence of HI never became first order in CF_3I. In the reactions in sealed tubes, reaction (14) was by far the main iodine producing reaction.

6) At pressures of CF_3I up to 0.5 mms, the initial split

$$CF_3I \longrightarrow CF_3 + I \qquad (1)$$

was not quite first order in CF_3I, the reaction being slightly pressure dependent. At a pressure of CF_3I of 0.1 mms. there was a slight inert gas effect. The rate of reaction under these conditions was also affected by the surface to volume ratio; no really satisfactory explanation has been found for this.

7) The activation energy of reaction (14) has been found to be 18.0 ± 1 K cals/mole

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (14)$$

If the activation energy of reaction (4)

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (4)$$

is taken to be 1 ± 1 K cals/mole, this yields a value for $D(CF_3-I)$ at 500°K of 55.5 ± 2 K cals/mole. This is in reasonable agreement with an approximate value of $D(CF_3-I) = 51 \pm 2$ K cals/mole derived from the temperature dependence of reaction (1)

$$C F_3 I \longrightarrow C F_3 + I \qquad (1)$$

This value of $D(CF_3-I) = 55.5 \pm 2$ K cals/mole. agrees with the lower limit of error of the value proposed by Farmer et alia[60] of 57 ± 4 K cals/mole. and with the upper limit of the value obtained by Dibeler, Reese and Mohler[78] of 48.5 ± 5 K cals/mole.

Appendix (i)

The Lindemann Mechanism of Unimolecular Reactions.

The mechanism for the activation of the reactant A is as follows:-

$$A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_3} \text{Products}$$

where A^* is a molecule with sufficient energy to decompose.

Setting up a stationary state for A^* , we obtain that

$$(A^*) = \frac{k_1 (A)^2}{k_2(A) + k_3}$$

whence $$\frac{-d(A)}{dt} = k_3 (A^*) = \frac{k_1 k_3 (A)^2}{k_2(A) + k_3}$$

Two extreme cases can be considered

(i) When $k_2(A) \ll k_3$. Deactivation of A^* is much greater than reaction, and

$$\frac{-d(A)}{dt} = \frac{k_1 k_3 (A)}{k_2}$$

This is the case at high pressure of A where the reaction is first order.

(ii) When $k_3 \ll k_2 (A)$. Reaction of A^* is much greater than its deactivation, and

$$\frac{-d(A)}{dt} = \frac{k_1 k_3}{k_3} (A)^2 = k_1 (A)^2$$

This is the case at low pressure of A where the reaction is second order.

The Efficiencies of Inert Gas in Transferring Energy.

The theory presented here is a simplified version of the method used by Johnston[40] . In the simple Lindemann theory, no account is taken of the effect of inert gases in transferring energy to the reacting molecule A. It is possible to treat this inert gas effect in a quantitative manner as follows:-

Let A be the reacting molecule and X,Y,---- inert gas molecules. Then the following reactions take place with the indicated rate constants:-

$$A + A \xrightarrow{k_1} A^* + A$$

$$A + X \xrightarrow{k_{1x}} A^* + X$$

$$A + Y \xrightarrow{k_{1y}} A^* + Y$$

- - - - - - - - - - - - - -

$$A^* + A \xrightarrow{k_2} A + A$$

$$A^* + X \xrightarrow{k_{2x}} A + X$$

$$A^* + Y \xrightarrow{k_{2y}} A + Y$$

- - - - - - - - - - - - - -

$$A^* \xrightarrow{k_3} \text{products.}$$

Setting up a stationary state for A* as before

$$(A^*) = \frac{k_1(A)^2 + k_{1x}(A)(X) + k_{1y}(A)(Y) + \text{----}}{k_3 + k_2(A) + k_{2x}(X) + k_{2y}(Y) + \text{----}}$$

and hence $\frac{-d(A)}{dt} = k_3(A^*) = \frac{k_3\left[k_1(A)^2 + k_{1x}(A)(X) + k_{1y}(A)(Y) + \cdots\right]}{k_3 + k_2(A) + k_{2x}(X) + k_{2y}(Y) + \cdots}$

and if we assume a unimolecular rate constant $\underline{k}$ for the decomposition of A, we have $\frac{-d(A)}{dt} = k(A)$

Under conditions where the rate of decomposition of (A^*) is much greater than its rate of deactivation,

$$k_3 \gg k_2(A) + k_{2x}(X) + k_{2y}(Y) + \cdots$$

and thus

$$\frac{-d(A)}{dt} = k(A) = k_1(A)^2 + k_{1x}(A)(X) + k_{1y}(A)(Y) + \cdots$$

$$\therefore k = k_1(A) + k_{1x}(X) + k_{1y}(Y) + \cdots$$

For a system consisting of the reacting gas A and one inert gas X, we have

$$k = k_1(A) + k_{1x}(X)$$

When the concentration of A is kept constant and the concentration of X is varied while still obeying the condition that

$$k_3 \gg k_2(A) + k_{2x}(X)$$

then, a graph of the assumed first order rate constant, $\underline{k}$, against the concentration of X should be a straight line. The slope of this line is k_{1x} and the intercept is $k_1(A)$. The efficiency, α_x, of the inert gas, X, in transferring energy to A relative to the efficiency of A = 1 is given by

$$\alpha_x = \frac{k_{1x}}{k_1}$$

Thus, from the graph of $\underline{k}$ against (X),

$$\alpha_x = \frac{\text{(slope of line) (Concentration of A)}}{\text{Intercept on } \underline{k} \text{ axis}}$$

From this argument, it is possible to show that a plot of $\frac{1}{k}$ against $\frac{1}{\text{effective pressure}}$ should give a straight line.

We have that

$$k\,(A) = \frac{k_3\left[k_1(A)^2 + k_{1x}(A)(X) + k_{1y}(A)(Y) + \text{----}\right]}{k_3 + k_2(A) + k_{2x}(X) + k_{2y}(Y) + \text{----}}$$

$$\frac{1}{k} = \frac{1}{k_1(A) + k_{1x}(X) + k_{1y}(Y) + \text{----}} + \frac{k_2(A) + k_{2x}(X) + k_{2y}(Y) + \text{---}}{k_3\ k_1(A) + k_{1x}(X) + k_{1y}(Y) + \text{---}}$$

Now $k_1(A) + k_{1x}(X) + k_{1y}(Y) + \text{----}$

$= k_1\left[(A) + \alpha_x(X) + \alpha_y(Y) + \text{----}\right]$

$= k_1\left[\text{effective pressure}\right]$

Thus a plot of $\frac{1}{k}$ against $\frac{1}{\text{effective pressure}}$ should be a straight line of slope $\frac{1}{k_1}$.

Appendix (ii)

The Dissociation of Iodine.

$$I_2 \rightleftharpoons I + I$$

Let P_I = pressure of iodine as atoms for total iodine present

p_I = actual pressure of iodine atoms

p_{I_2} = actual pressure of iodine molecules

$\therefore P_I = p_I + 2p_{I_2}$

If the fraction dissociated = a

$$p_I = a \quad P_I$$

and $$p_{I_2} = \frac{(1 - a) P_I}{2}$$

$$Kp = \frac{p_I \, p_I}{p_{I_2}} = \frac{a^2 P_I^2}{(\frac{1-a}{2}) P_I} = \frac{2a^2 P_I}{1-a}$$

$$\therefore \log Kp = \log \frac{a^2}{1-a} + \log P_I + \log 2 \text{ -------- (i)}$$

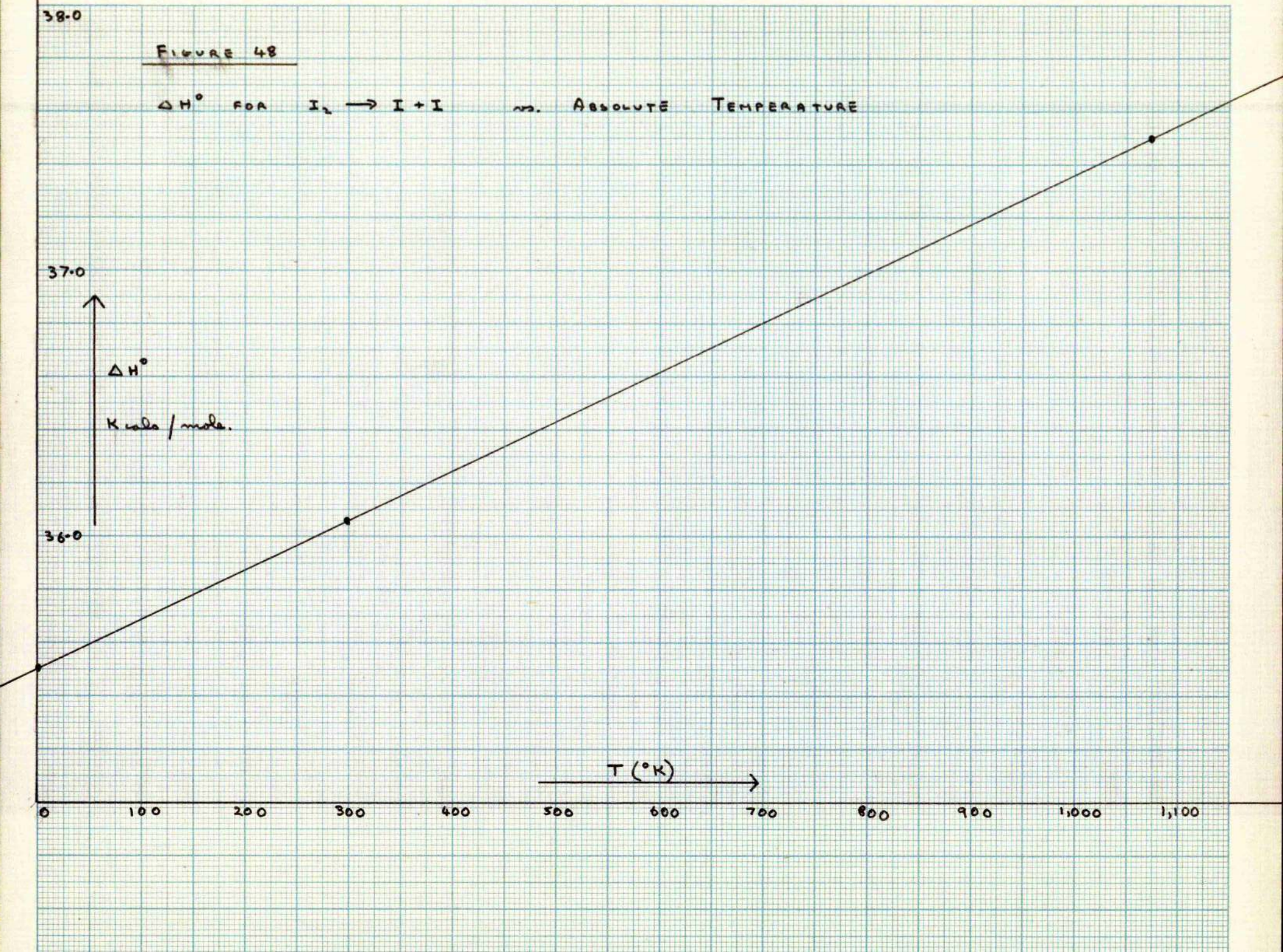
Equation (i) may therefore be solved for $\log \frac{a^2}{1-a}$ for a given P_I if Kp is known.

The most accurate data on the dissociation of iodine is probably that due to Perlman and Rollefson[127]. From their results, together with free energy function values calculated from spectroscopic data, it is possible to derive a value of Kp at any temperature within the range 0°K to 1,500°K. If it is assumed that ΔH° for the reaction

$$I_2 \longrightarrow I + I$$

FIGURE 48

ΔH° FOR $I_2 \longrightarrow I + I$ vs. ABSOLUTE TEMPERATURE



is constant over the temperature range 872°K to 1274°K, it can be derived from their data that

$$\Delta H^{\circ}_{1073} = 57{,}500 \text{ cals./mole.}$$

They also give $\Delta H^{\circ}_{298} = 56{,}057$ cals./mole.

$\Delta H^{\circ}_{0} = 55{,}514$ cals./mole.

This variation of ΔH° with temperature is shown in figure 48. Since a straight line is obtained in figure 48,

$$\frac{d\,\Delta H^{\circ}}{dT} = \text{constant}$$

That is $$\Delta H^{\circ} = \Delta H^{\circ}_{o} + b\,T$$

where b is a constant.

Therefore, on integration of the equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2}$$

we obtain $$\ln K = \frac{-\Delta H^{\circ}_{o}}{RT} + \frac{b}{R} \ln T + I$$

where I is an integration constant.

Now, from the slope of the line in figure 48, we obtain

$b = 1.85$ cals/C°.

$$\ln K = \frac{-\Delta H^{\circ}_{o}}{RT} + \frac{1.85}{R} \ln T + I$$

$$\text{or } \log K - 0.955 \log T = \frac{-\Delta H^{\circ}_{o}}{4.57T} = J$$

where $J = \frac{I}{2.303}$

Thus, a graph of $\log K - 0.955 \log T$ against $\frac{1}{T}$ should be a straight line of slope $-\Delta H^{\circ}_{o} / 4.57$.

The results of treating Perlman and Rollefson's data in this manner are listed below:

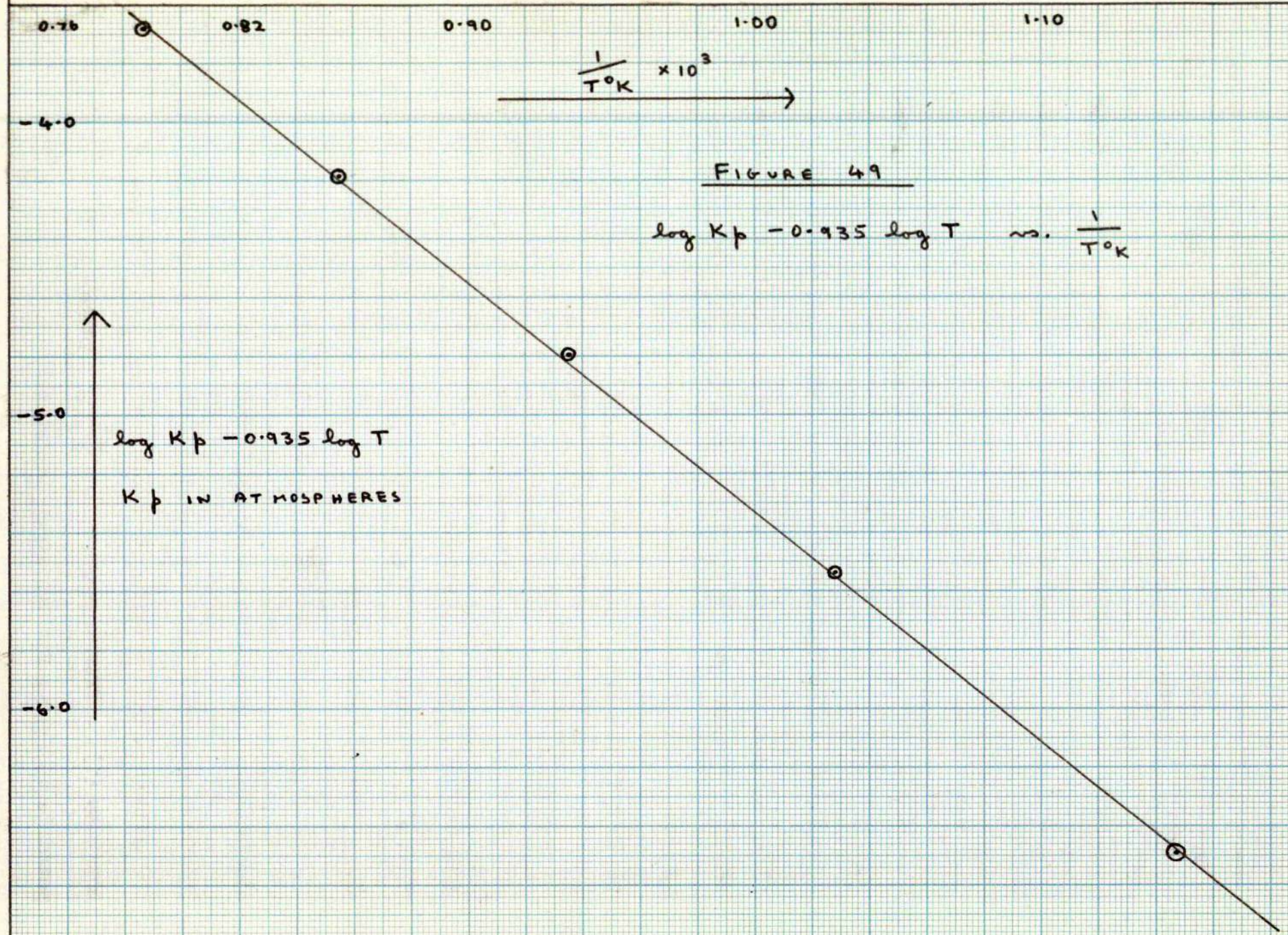


FIGURE 49

$\log K_p - 0.935 \log T$ vs. $\frac{1}{T°K}$

Temperature (°K)	Log Kp Kp in atmospheres	Log Kp - 0.955 log T	$\frac{1}{T^{\circ}K} \times 10^5$
1274	- 0.7747	- 5.680	0.787
1173	- 1.315	- 4.184	0.855
1073	- 1.964	- 4.797	0.955
973	- 2.745	- 5.559	1.028
872	- 3.738	- 6.487	1.147

These data are plotted in figure 49. From figure 49, ΔH°_{o} = 55,600 cals/mole in reasonable agreement with the value of 55,514 cals/mole derived by Perlman and Rollefson using another method.

At 1073°K,

$$\log Kp - 0.955 \log T = - 4.797$$

$$\frac{\Delta H^{\circ}_{o}}{4.57T} = \frac{55,514}{4.57.1073} = 7.24$$

Therefore J = 7.24 - 4.80 = 2.44

Thus at any temperature within the range 0°K to 1300°K, log Kp may be found from the expression

$$\log Kp = \frac{-55,514}{4.57T} + .955 \log T + 2.44$$

This value of Kp is in atmospheres.

Since Kp in atmospheres is known and P_I may be evaluated in atmospheres, it is possible to calculate $\log \frac{a^2}{1 - a}$ by use of equation (i). From a graph of $\log \frac{a^2}{1 - a}$ against a, it is then possible to find a for the given conditions.

Appendix (iii)

Integration of $\frac{dx}{dt} = C_2' (a-x)(x)^{\frac{1}{2}}$

$$\frac{dx}{(a-x)\ (x)^{\frac{1}{2}}} = C_2' \, dt$$

Let $x = y^2$ then $dx = 2y\ dy$

$$\frac{2y\ dy}{(a-y^2)(y)} = C_2' \, dt$$

$$\frac{2\ dy}{(a - y^2)} = C_2' \, dt$$

$$\int_{y\ \text{initial}}^{y\ \text{final}} \frac{2\ dy}{(a - y^2)} = \int_{o}^{t} C_2' \, dt$$

$$\frac{2.303}{\sqrt{a}} \left(\log \frac{\sqrt{a} + y\ \text{final}}{\sqrt{a} - y\ \text{final}} - \log \frac{\sqrt{a} + y\ \text{initial}}{\sqrt{a} - y\ \text{initial}} \right) = C_2' \, t$$

$$C_2' = \frac{2.303}{t\ \sqrt{a}} \left(\log \frac{\sqrt{a} + \sqrt{x}\ \text{final}}{\sqrt{a} - \sqrt{x}\ \text{final}} - \log \frac{\sqrt{a} + \sqrt{x}\ \text{initial}}{\sqrt{a} - \sqrt{x}\ \text{initial}} \right)$$

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